CA20N EV 805 1988 Mai c.2



METHYL BROMIDE STRUCTURAL FUMIGATION PROCEDURES

Agricultural and Industrial Chemicals Section Hazardous Contaminants Coordination Branch

ONTARIO MINISTRY OF THE ENVIRONMENT



This publication has been endorsed by the Ontario Pesticides Advisory Committee.

Revised February 1988

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REQUIREMENTS FOR SPACE FUMIGATION

Following Agriculture Canada's re-evaluation of the registered fumigants, and the publication of air quality guidelines established by the Ontario Ministry of the Environment, the following information must be submitted with applications for a permit to conduct space fumigations with methyl bromide and phosphine in Ontario.

- A diagram to scale showing property lines, and the position and use of buildings adjacent to the building(s) to be fumigated.
- 2. The names and licence numbers of all personnel carrying out the fumigation (N.B. Section 28(1) of the Regulation under the <u>Pesticides Act</u> requires that a Structural Class 2 or Class 1 <u>Licenced Exterminator must assist the Structural 1</u> Exterminator who signed the permit application).
- 3. The name and telephone number of a contact person responsible for the building(s) to be fumigated.
- 4. The local Medical Officer of Health and the local police and fire departments must be notified of the time and place of fumigation. These agencies must also be notified when the fumigation has been completed.
- 5. Fumigant levels and temperature must be monitored within the building during fumigation. The method of monitoring is left to the discretion of the exterminator. This will vary with building design, duration of fumigation, etc. Monitoring data must be submitted with the confirmation letter within 7 days after completing the fumigation.
- 6. Aeration cannot be carried out under inversion conditions. Inversions are most likely to occur during summer and winter from 1:00 a.m. to 8:00 a.m. During the winter, inversions are also likely to occur during early afternoon. Information on weather conditions can be obtained on a 24-hour basis for eastern Ontario by calling the Toronto Weather Office at (416) 676-3020 and for northwestern Ontario, by calling the Winnipeg Weather Office at (204) 949-2071.
- During aeration, the exterminator must ensure that no personnel or by-standers are located downwind in the fumigant plume.
- 8. Aeration may be staged depending upon requirements from the Ontario Ministry of the Environment. Aeration procedure will vary with building design, location and proximity to residential areas.

PREFACE

PRINCIPLES OF FUMIGATION

FACTORS AFFECTING FUMIGANTS*

Choice of Fumigant

There are many chemical compounds which are volatile at ordinary temperatures and sufficiently toxic to fall within the defintion of fumigants. In actual practice, however, most gases have been eliminated owing to unfavourable properties, the most important being chemical instability and destructive effects on materials. Damage to materials may take place in several ways, as follows:

- Excessively corrosive compounds attack shipping containers or spoil
 the structure and fittings of fumigation chambers or other spaces
 undergoing treatment.
- Reactive chemicals form irreversible compounds, which remain as undesirable residues in products. In foodstuffs such reactions may lead to taint or the formation of poisonous residues. Other materials may be rendered unfit by visible staining or by the production of unpleasant odours.
- 3. Physiologically active compounds may destroy or severely injure growing plants, fruit or vegetables, and may adversely affect seed germination.

Highly flammable compounds are not necessarily excluded if dangers of fire and explosion can be controlled by the addition of other suitable compounds, or if fumigation procedures are carefully designed to eliminate these hazards. Toxicity to human beings is not necessarily a cause for exclusion. All known fumigants are toxic to humans to a greater or lesser degree and ways can be devised for their safe handling under the required conditions of application. However, some commonly used compounds have been shown to be capable of producing long-term effects that were previously unknown. The use of such fumigants is becoming more restricted and some materials have already been eliminated from the list of fumigants approved for use in certain countries.

* This section is printed with permission from the Food and Agriculture Organization of the United Nations from FAO Plant Production and Protection Paper 54: Manual of Fumigation for Insect Control by E.J. Bond, 1984.

Evaporation of Fumigants

BOILING POINT

The boiling point of different chemical compounds generally rises with the increase of molecular weights. This generalization is borne out by the data for the fumigants shown in Figure 1, where molecular weights are plotted against boiling points. The relationship stated above holds very well, except for methyl bromide, and it demonstrates that important compounds, such as carbon tetrachloride or ethylene dibromide, will evaporate very slowly under practical fumigation conditions. If the highest possible concentrations are required at the beginning of the fumigation with such compounds, more rapid volatilization will have to be effected in some way.

Figure 1 shows that, from the physical standpoint, fumigants may be divided into two main groups according to whether they boil above or below room or moderate outdoor temperatures (20°C to 25°C). The low boiling point fumigants, such as methyl bromide, may be referred to as gaseous -type fumigants. These are kept in cylinders or cans designed to withstand the pressure exerted by the gas at the highest indoor or outdoor temperatures likely to be encountered.

The second main group of fumigants contains those with high boiling points; these are usually described as liquid-type or solid-type according to the form in which they are shipped and handled. In some kinds of work, such as grain and soil fumigation, the slow evaporation of certain liquids is an advantage because the initial flow leads to a better distribution of the gas subsequently volatilized. In other applications, where personnel have to distribute the fumigants, slow evaporation of the liquids or solids makes them safer to handle.

Included in the general term solid-type fumigants are certain materials which are not fumigants themselves, but which react to form fumigants after application. Examples are calcium cyanide powder, which reacts with atmospheric moisture to yield hydrogen cyanide (HCN), and formulations of aluminium and magnesium phosphides which also react with moisture to produce phosphine (hydrogen phosphide).

There are also some fumigants in the form of crystals and flakes that sublime to give off fumigant vapours. Examples are paradichlorobenzene and naphthalene.

MAXIMUM CONCENTRATIONS

The maximum weight of a chemical that can exist as a gas in a given space is dependent on the molecular weight of that chemical. This fact, implicit in the well-known hypothesis of Avogadro, has an important practical application. It is useless attempting to volatilize in an empty chamber more fumigant than can exist in the vapour form. Table 2 shows the maximum amounts of a number of fumigants that can be vaporized in a given space. It will be noted that the fumigants with low boiling points, such as methyl bromide or ethylene oxide, may be released in large amounts compared with high boiling point compounds, such as naphthalene and paradichrorobenzene. The data in Table 2, while useful for

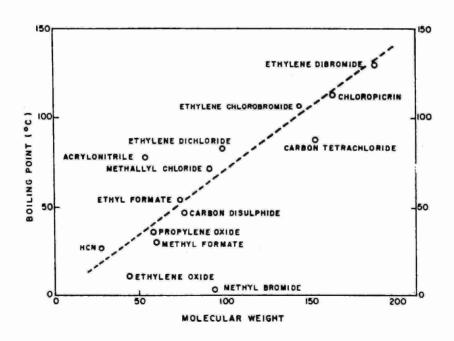


FIGURE 1. - Relationship between molecular weight and boiling point of some fumigants.

TABLE 2. - MAXIMUM WEIGHTS OF VARIOUS FUMIGANTS WHICH CAN EXIST IN VAPOUR FORM IN AN EMPTY FUMIGATION SPACE AT DIFFERENT TEMPERATURES 1

| Fumigant | Maximum weight, in grammes/cubic metre ² at indicated temperatures | | | | | | | | | | |
|------------------------|---|---------------|----------------|----------------|----------------|----------------|----------------|----------------|--|--|--|
| | 0°C (32°F) | 5°C (41°F) | 10°C (50°F) | 15°C (59°F) | 20°C (68°F) | 25°C (77°F) | 30°C (86°F) | 35°C (95°F) | | | |
| Acrylonitrile | 102.6 | 129.8 | 164.4 | 206.3 | 252.9 | 319.1 | 397.8 | 482.4 | | | |
| arbon disulphide | 568.1 | 701.1 | 843.7 | 1 010.9 | 1 297.2 | 1 430.8 | 1 740.9 | 2 096.3 | | | |
| Carbon tetrachloride . | 288.5 | 363.0 | 460.9 | 572.6 | 730.9 | 916.8 | 1 145.4 | 1 398.5 | | | |
| Chloropicrin | 57.8 | 79.5 | 108.7 | 139.5 | 179.5 | 220.6 | 277.8 | 358.7 | | | |
| Dichlorvos (DDVP) | 0.02 | 0.03 | 0.05 | 0.08 | 0.13 | 0.21 | 0.32 | 0.48 | | | |
| thylene dibromide | 30.5 | 54.1 | 63.7 | 83.5 | 112.8 | 141.2 | 173.6 | 214.7 | | | |
| thylene dichloride | 133.4 | 173.7 | 223.7 | 282.0 | 350.1 | 430.3 | 537.1 | 668.2 | | | |
| thylene oxide 1 | 331.5 | 1 606.6 | 1 854.5 | 1 862.4 | 1 830.4 | 1 800.0 | 1 771.2 | 1 740.8 | | | |
| lydrogen cyanide | 418.7 | 532.0 | 643.4 | 751.3 | 900.4 | 1 072.2 | 1 084.7 | 1 067.7 | | | |
| ethyl bromide 3 | 839.3 | 4 152.8 | 4 079.4 | 4 008.6 | 3 940.2 | 3 874.1 | 3 810.1 | 3 748.3 | | | |
| Saphthalene | 0.15 | 0.22 | 0.33 | 0.43 | 0.56 | 0.69 | 0.95 | 1.40 | | | |
| aradichlorobenzene | 0.69 | 1.61 | 2.49 | 3.18 | 5.14 | 7.89 | 11.64 | 17.56 | | | |
| hosphine 1 | 514.4 | 1 487.2 | 1 460.9 | 1 435.5 | 1 411.0 | 1 387.4 | 1 364.5 | 1 342.3 | | | |
| ulphuryl fluoride 4 | 546.0 | 4 464.2 | 4 385.3 | 4 309.2 | 4 235.7 | 4 164.6 | 4 095.9 | 4 029.4 | | | |
| arbon dioxide 1 | 959.8 | 1 924.6 | 1 890.6 | 1 857.8 | 1 826.1 | 1 795.4 | 1 765.8 | 1 737.1 | | | |

 $^{^{1}}$ Values calculated from formulas derived by Roark and Nelson (1929). 2 Equivalent to milligrammes per litre, or ounces (avoirdupois) per 1 000 cubic feet.

comparative purposes, apply only to empty spaces. Sorption of the fumigant by the material treated in a given space will permit greater amounts to be volatilized. Nevertheless, the figures given will still apply to the amount which can exist as vapour in the free air space surrounding the fumigated material.

LATENT HEAT OF VAPORIZATION

Unless it is sustained by warming from an outside source, the temperature of an evaporating liquid constantly drops owing to the fall in energy caused by the escape of molecules with greater than average energy. Thus, evaporation takes place at the expense of the total heat energy of the liquid. The number of calories lost in the formation of one gramme of vapour is called the latent heat of vaporization of the liquid. Some fumigants have higher latent heats than others.

Both HCN and ethylene oxide, with latent heats of 210 and 139 respectively, absorb considerably more heat in passing from liquid to vapour than do methyl bromide and ethylene dibromide, with latent heats of 61 and 46 respectively.

The factor of latent heat is of important practical significance. The high pressure fumigants, such as HCN, ethylene oxide and methyl bromide, are usually kept under pressure in suitable cylinders or cans. On release into the atmosphere, volatilization takes place rapidly and, unless the lost heat is restored, the temperature of the fumigant may fall below the boiling point and gas may cease to be evolved. Also, as the liquid changing to gas is led through metal pipes and tubes, or rubber tubing, the fall in temperature may freeze the fumigant in the lines and prevent its further passage. In many applications, to be described elsewhere in this manual, it is advisable to apply heat to the fumigant as it passes from the container into the fumigation space.

Fumigants that are liquids at normal temperatures and are volatilized from evaporating pans or vaporizing nozzles may require a source of heat, such as a hot plate, in order that full concentrations may be achieved rapidly.

Diffusion and Penetration

As stated above, fumigants are used because they can form insecticidal concentrations: (a) within open structures or (b) inside commodities and in cracks and crevices into which other insecticides penetrate with diffculty or not at all. Hence, it is necessary to study the factors that influence the diffusion of gases in every part of a fumigation system. This study includes the behaviour of fumigants both in empty spaces and also in structures loaded with materials into which the gas is required to penetrate.

LAW OF DIFFUSION

Graham's law of diffusion of gases states that the velocity of diffusion of a gas is inversely proportional to the square root of its density.

Also, the densities of gases are proportional to their molecular weights. Therefore, a heavier gas, such as ethylene dibromide, will diffuse more slowly throughout an open space than a lighter one such as ethylene oxide. While this basic law is of importance, especially for empty space fumigations, the movement of gases in contact with any internal surface of the structure or within any contained materials is greatly modified by the factor of sorption discussed below.

The rate of diffusion is also directly related to temperature, so that a given gas will diffuse more quickly in hot air than in cold air.

SPECIFIC GRAVITY AND DISTRIBUTION

Many of the commonly used fumigants are heavier than air. A notable exception is hydrogen cyanide. If a gas heavier than air is introduced into a chamber filled with air and it is not agitated by fans or other means, it will sink to the bottom and form a layer below the air. The rate of mixing between the two layers may be very slow. For example, in a fumigation of the empty hold of a ship with the heavy gas methyl bromide where the fumigator had neglected to place a circulating fan, a sharp demarcation was observed between the lower half with the gas, where all of the insects were killed, and the upper part, where complete survival occurred (Monro et al, 1952).

In good fumigation practice, settling or stratification will not be encountered if adequate provision is made to disperse the gas properly from the very beginning of the treatment. Even distribution can be ensured by employing singly or in suitable combination: multiple gas inlets, fans or blowers and/or circulation by means of ducts and pipes. Contrary to popular belief, once a gas or number of gases heavier than air have been thoroughly mixed with the air in a space, settling out or stratification of the heavier components takes place very slowly; so slowly, in fact, that once a proper mixture with air has been secured, the problem of stratification of a heavier-than-air fumigant is of no practical importance for the exposure periods commonly used in fumigation work.

MECHANICAL AIDS TO DIFFUSION

It has already been suggested that distribution and penetration can be aided and hastened by the use of blowers and fans. Such propellers may work free in the structure or through a system of circulating ducts. These devices may also add greatly to the efficiency of the fumigation process by hastening the volatilization of high boiling point liquids from evaporating pans and by preventing stratification of heavy gases. Also, a factor known as the Turtle effect* has proved useful in the fumigation of certain materials susceptible to injury. It was shown that rapid stirring by a centrifugal fan in a fumigation chamber at atmospheric pressure greatly hastened the attainment of uniform concentrations

^{*} This effect was first demonstrated by E.E.Turtle (Ph.D.thesis), University of London 1941.

of methyl bromide in all parts of a load of early potatoes, so that the consignment was not overdosed at the outside of the packages or underdosed at the centre (Lubatti and Bunday, 1958). In a four-hour exposure period, rapid stirring for one hour at the beginning of the treatment was, to all intents and purposes, as effective as continuous stirring for the whole time.

SORPTION

A very important factor affecting the action of fumigants is the phenomenon known as sorption. It is not possible in this manual to give a complete explanation of sorption, because the interaction of all forces involved is complex. Fortunately, for the purpose of understanding fumigation practice, it is possible to give a general account of the important factors concerned.

In the relationship of gases to solids, sorption is the term used to describe the total uptake of gas resulting from the attraction and retention of the molecules by any solid material present in the system. Such action removes some of the molecules of the gas from the free space so that they are no longer able to diffuse freely throughout the system or to penetrate further into the interstices of the material. fumigation practices, collision with air molecules tends to slow down gaseous diffusion through the material and sorption takes place Thus, there is a progressive rather than immediate lowering of the concentrations of the gas in the free space. This gradual fall in concentration is illustrated in the graphs in Figure 2. The curves for the four compounds clearly show the differences in degree of each of sorption of the fumigants by the same load in the chamber. Throughout the exposure period of six hours, the fall in concentration of methyl bromide was proportionately less compared with that for the three other fumigants, both in the empty chamber and with the two loads of oranges. This was due to the fact that the internal surface of the chambers and the boxes of oranges both sorbed less of the methyl bromide than of the other gases in proportion to the applied dosage. Sorption under a given set of conditions determines the dosage to be applied, because the amount fumigant used must be sufficient both to satisfy the total sorption during treatment and also to leave enough free gas to kill the pest organisms.

The general term sorption covers the phenomena of adsorption and absorption. These two are reversible because the forces involved, often referred to as van der Waal's forces, are weak. On the other hand, a stronger bonding called chemisorption usually results in chemical reaction between the gas and the material and is irreversible under ordinary circumstances (Berck, 1964).

Physical Sorption

From the point of view of practical fumigation, adsorption and absorption, being both physical in nature and reversible, may be

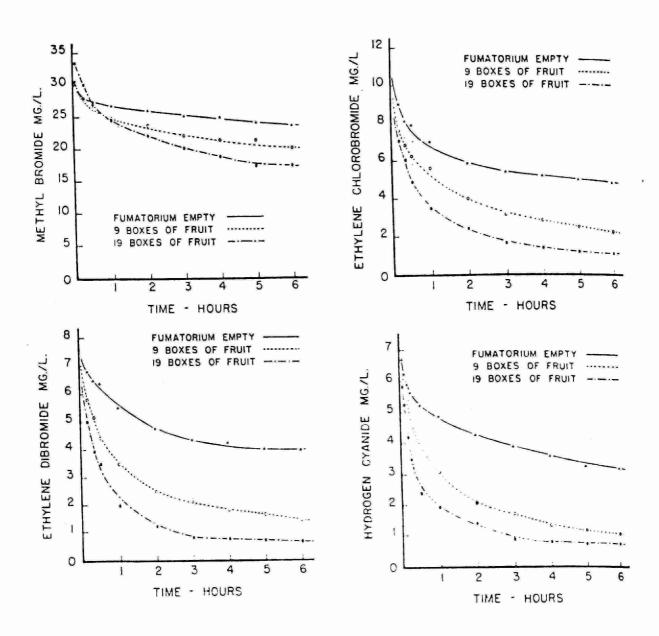


FIGURE 2. - Relationship between load (boxes of oranges) and concentration of fumigant in gas phase in a 3-cubic-metre chamber at atmospheric pressure and 21°C (Sinclair and Lindgren, 1958).

discussed in this manual under the heading of physical sorption. However, it is necessary to make some distinction between them at the outset because the forces involved may be less with adsorption than with absorption.

Stated briefly, adsorption is said to occur when molecules of a gas remain attached to the surface of a material. Because some adsorbents, such as charcoal or bone meal, are highly porous bodies with large internal surfaces, adsorption may also occur inside a given body.

Absorption occurs when the gas enters the solid or liquid phase and is held by capillary forces that govern the properties of solutions. For instance, a gas may be absorbed in the aqueous phase of grain or in the lipid phase of nuts, cheese or other fatty foods (Berck, 1964).

Physical sorption, considered generally, is an extremely important factor affecting the successful outcome of fumigations. Apart from specific reactions between certain gases and commodities, it may be stated as a general rule that those fumigants with higher boiling points tend to be more highly sorbed than the more volatile compounds. This is illustrated in the graphs in Figure 2; with this particular load there is greater sorption of ethylene dibromide (boiling point 131° C) and of hydrogen cyanide (boiling point 26° C) than of methyl bromide (boiling point 3.6° C). (The considerable difference in the sorption of hydrogen cyanide and methyl bromide is due to factors other than boiling point or molecular weight.)

Physical sorption varies inversely as the temperature, and is thus greater at lower temperatures. This fact has important practical applications. It is one of the reasons why dosages have to be progressively increased as the temperature of fumigation is lowered (Figure 3).

Sorption may also be influenced by the moisture content of the commodity being fumigated. This was demonstrated by Lindgren and Vincent (1962) in the fumigation of a number of foodstuffs with methyl bromide; at higher moisture contents more fumigant was sorbed. This effect may be important with fumigants which are soluble in water to any significant degree.

The specific physical reaction between a given gas and a given commodity cannot be accurately predicted from known laws and generalizations. Usually, a certain fumigant must be tested with each material concerned before a recommendation for treatment can be drawn up.

Desorption

When a treatment is completed and the system is ventilated to remove the fumigant from the space and the material, the fumigant slowly diffuses from the material. This process is called desorption and is the reverse of physical sorption. With the common fumigants and the commodities usually treated, residual vapours are completely dissipated within reasonable periods, although the length of time varies considerably according to the gas used and the material treated. Because of the inverse effect of temperature, dissipation of the fumigant usually takes place more slowly when the material is cold and may be hastened by warming the space and its contents.

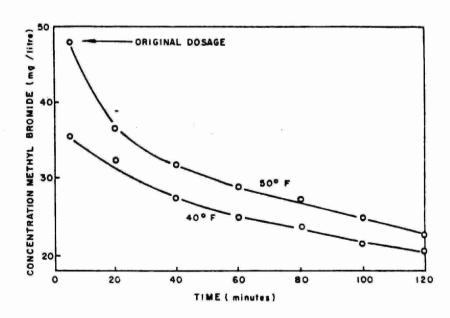


FIGURE 3. - Effect of temperature on sorption of fumigant by identical loads (weights) of peaches. The same dosage of 48 g per m³ of methyl bromide was applied in each treatment. (Dumas and Monro, 1966)

Humidity also facilitates desorption of fumigants; at high humidity, wheat fumigated with ethylene dibromide was found to desorb 80 percent more of the fumigant than at very low humidity (Dumas and Bond, 1979). As humidities can change appreciably with changing temperature, the rate of desorption may be dependent on the combined effect of both factors.

Removal of desorbing gas can be speeded up by employing fans and blowers to force fresh air through the material. Natural ventilation may be hastened by taking the goods out of doors where advantage can be taken of wind, thermal air currents and the warming effect of sunlight.

Some of the residual fumigant, usually small in quantity, may not be desorbed because of chemical reaction with the material.

CHEMICAL REACTION

If chemical reaction takes place between the gas and the material, new compounds are formed. This reaction is usually characterized by specificity and irreversibility. If the reaction is irreversible, permanent residues are formed. Examples are the reaction between hydrogen cyanide (HCN) and the reducing sugars in dried fruits with the formation of cyanohydrins (Page and Blackith, 1956) or the appearance of inorganic bromide compounds after treatment of some foodstuffs with methyl bromide (McLaine and Monro, 1937).

Because this type of reaction is essentially chemical it may be expected that its intensity varies directly with the temperature. This assumption has been confirmed by observation. Dumas (1973) has reported proportionately less fixed bromide residues in fruits as the temperature of fumigation was reduced from 25 to 4°C . Lindgren et al (1962) found an increase in the bromide content of wheat as the temperature during fumigation rose from 10 to 32°C .

Significance of Residues in Foods

RESIDUE TOLERANCES

In recent years attention has been focussed on the nature and possible effects on human beings of insecticidal residues appearing in foodstuffs. World-wide interest in this problem is reflected in the fact that international organizations such as the Food and Agriculture Organization the United Nations (FAO) and the World Health Organization (WHO) have special committees to investigate and report on the nature and significance of residues formed in foodstuffs as the result of the application of pesticides at different stages (as seed dressings, during growth, storage, transportation, etc.) prior to human consumption. These special committees review a number of pertinent factors involved in the use of each pesticide. Important factors, among others, are the toxicological significance of any residues formed and the average fraction of total diet likely to be constituted by a food containing this Through their Codex Alimentarius Committee these organizations residue. undertake "to recommend international tolerances for pesticide residues in specific food products."

Such recommendations are not binding on Member Nations of these organizations but are intended to be used as guides when particular countries are formulating their own regulations for pesticide residue tolerances.

Fumigants may form residues when used on foodstuffs for insect control.

CANADA

The Food and Drugs Act:

In this Act, "food" includes any article manufactured, sold or represented for use as food or drink for man, chewing gum, and any ingredient that may be mixed with food for any purpose whatever.

Part I. Food. Section 4.

- 4. No person shall sell an article of food that
- (a) has in or upon it any poisonous or harmful substance:
- (b) is unfit for human consumption;
- consists in whole or in part of any filthy, putrid, disgusting, rotten decomposed or diseased animal or vegetable substance;
- (d) is adulterated; or
- (e) was manufactured, prepared, preserved, packaged or stored under unsanitary conditions.

Part II. Regulations. Section 25(1)(a)

- 25. (1) The Governor in Council may make regulations for carrying the purposes and provisions of this Act into effect, and, in particular, but not so as to restrict the generality of the foregoing, may make regulations
 - declaring that any food or drug or class of food or drugs is adulterated if any
 prescribed substance or class of substances is present therein or has been added
 thereto or extracted or omitted therefrom;

The Food and Drug Regulations:

Part B. Foods, Division 1

B.01.001. In this Part "agricultural chemical" means any substance that

- is used or represented for use in or upon a food during production, storage or transport, or
- (b) has been registered under the Pest Control Products Act

and the use of which results or may reasonable be expected to result in a residue of such substance or a derivative thereof in or upon foods, and includes any pesticide, plant growth regulator, fertilizer, adjuvant, carrier or ingredient used with such a substance, but does not include any

- (c) food additive, other than those listed in the tables to Division 15,
- (d) nutritive material that is used, recognized or commonly sold as an article or inggedient of food,
- (e) vitamin, mineral nutrient or amino acid,
- spice, seasoning, flavouring preparation, essential oil, oleoresin or natural extractive,
- (g) food packaging material or component thereof, or
- (h) drug recommended for administration to animals that may be consumed as food;
- B.01.046. (1) A food is adulterated if any of the following substances or classes of substances are present therein or have been added thereto:
 - (n) ethylene thiourea
 - (p) chloring ed dibenzo-p-dioxins

Division 15 Adulteration of Food

- B.15.002. (1) Subject to subsections (2) and (3), a food is adulterated if an agricultural chemical or any of its derivatives is present therein or has been added thereto, singly or in any combination, in an amount exceeding 0.1 part per million, unless it is listed and used in accordance with the tables to Division 16.
 - (2) Subject to subsection (3), a food is exempt from paragraph 4(d) of the Act if the only agricultural chemicals that are present therein or have been added thereto are any of the following:
 - (e) a fertilizer;
 - (b) an adjuvant or a carrier of an agricultural chemical;
 - (c) an inorganic bromide salt;
 - (d) silicon dioxide;
 - (e) sulphur; or
 - (f) viable spores of Bacillus thuringiensis Berliner.
 - (3) A food named in column IV of an item of Table II to this Division is exempt from paragraph 4(d) of the Act if the agricultural chemicals named in columns I and II of that item are present therein or have been added thereto in an amount not exceeding the limit, expressed in parts per million, set out in column III of that item for that food.

A comprehensive review of fumigant residues has been given by Lindgrer $\underline{\text{et}}$ al (1968).

Other Effects on Materials

Apart from the question of significant residues in foodstuffs, there is the problem of other effects which have a direct bearing either on the choice of the particular fumigant or on the decision as to whether fumigation is possible at all. The main types of reaction may be summerised as follows:

PHYSIOLOGICAL EFFECTS

1. Nursery Stock and Living Plants

- (a) Stimulation of growth
- (b) Retardation of growth
- (c) Temporary injury and subsequent recovery
- (d) Permanent injury, usually followed by death

Seeds

- (a) Stimulation of germination
- (b) Impairment or total loss of germination
- (c) Poor growth of seedlings from germinated seeds

3. Fruit and Vegetables

- (a) Visible lesions
- (b) Internal injury
- (c) Shortening of storage life
- (d) Delay of ripening
- (e) Stimulation of storage disorders

4. Infesting Organisms

- (a) Death
- (b) Stimulation of growth or metamorphosis
- (c) Delay in development
- (d) Stimulation of symptoms of disease (so-called "diagnostic effect")

PHYSICAL AND CHEMICAL EFFECTS ON NONLIVING MATERIALS

- Production of foul or unpleasant odours in furnishings or materials stored in premises.
- Chemical effects that spoil certain products (for example, some fumigants render photographic films and papers unusable).
- Reaction with lubricants followed by stoppage of machinery (clocks will often stop after fumigation with HCN).
- 4. Corrosive effects on metals (phosphine reacts with copper, particularly in humid conditions).

Dosages and Concentrations

There should be a clear understanding of the difference between dosage and concentration.

The dosage is the amount of fumigant applied and is usually expressed as weight of the chemical per volume of space treated. In grain treatments, liquid-type fumigants are often used and the dosage may be expressed as volume of liquid (litres or gallons) to a given volume (amount of grain given as litres or bushels) or sometimes to a given weight (quintals, metric tonnes or tons).

From the moment that a given dosage enters the structure being fumigated, molecules of gas are progressively lost from the free space either by the process of sorption and solution described above or by actual leakage from the system, if this occurs. The concentration is the actual amount of fumigant present in the air space in any selected part of the fumigation system at any given time. The concentration is usually determined by taking samples from required points and analysing them. It may thus be said that the dosage is always known because it is a pre-determined quantity. Concentration has to be determined because it varies in time and position according to the many modifying factors encountered in fumigation work.

Three methods of expressing gas concentrations in air are in common use: weight per volume, parts by volume and percent by volume.

WEIGHT PER VOLUME

For practical designation of dosages, this is the most convenient method because both factors - the weight of the fumigant and the volume of the space - can be easily determined. In countries using the metric system, this is usually expressed in grammes per cubic metre (g/m^3) , whereas in countries using the British system of weights and measures, expression is usually in terms of pounds or ounces avoirdupois (avdp) per 1 000 cubic feet $(1b/1\ 000\ ft^3\ or\ oz/1\ 000ft^5)$.

By a fortunate coincidence in units of measurement, grammes per cubic metre are, for all practical purposes, equal to ounces per thousand cubic feet. Thus, recommended dosages can readily be converted from one system

to the other*.

In reports of laboratory experiments, dosages and concentrations are usually given in milligrammes per litre (mg/l), equivalent to grammes per cubic metre.

PARTS OR PERCENT BY VOLUME

Parts by volume and percent by volume will be discussed together because both modes of expression give the relative numbers of molecules of gas present in a given volume of air. The values for both modes have the same digits, but the decimal points are in different places (3 475 parts per million by volume of a gas is the same as 0.3475 percent by volume).

Parts per million of gases in air are used in human and mammalian toxicology and in applied industrial hygiene. Percent by volume is used in expressing the flammability and explosive limits of gases in air.

CALCULATIONS FOR CONVERSION OF CONCENTRATION VALUES

By means of simple calculations giving useful approximations, values may be converted from weight per volume to parts by volume and vice versa. These calculations take into account the molecular weight of the gas and the fact that, with all gases, the gramme molecular weight of the substance occupies 22.414 litres at 0°C and 760 millimetres pressure. (If precise values are needed for the other temperatures and pressures, corrections for absolute temperature and pressure may be made in the usual manner.)

Hence 1 ounce per 1 000 cubic 'feet:

$$=\frac{28.35}{28.316}$$
 × 1 000 grammes per 1 000 litres

$$= \frac{28.35}{28.316} \times \frac{1\ 000\ \text{grammes}}{1\ 000} \text{ per cubic metre}$$

^{*} One ounce (avoirdupois)=28.35 grammes. One cubic foot=28.316 litres.

^{= 1.002} grammes per cubic metre

- A. To convert grammes per cubic metre (or milligrammes per litre or ounces per 1 000 cubic feet) into parts by volume.
 - 1. Divide the given value by the molecular weight of the gas and multiply by 22.4; the resulting figure is the number of cubic centimetres (cm³) of gas per litre of air.
 - 2. One thousand times the figure obtained is the value in parts per million by volume.
 - One tenth of the figure obtained in (1) is the percentage by volume.

Example. To convert lg/m³ of PH₃ (molecular weight 34 approximately)

= $.659 \text{ cm}^3 \text{ per litre}$

 $\frac{1 \times 22.4}{34} = 659 \text{ parts per million by volume approximately}$ = .0659% by volume approximately

- B. To convert parts per million (or percentage of volume) of gases to grammes per cubic metre (or milligrammes per litre or ounces per 1 000 cubic feet):
 - Divide the parts per million by 1 000, or multiply the percentage by ten to give the number of cubic centimetres of gas per litre of air.
 - Multiply this figure by the molecular weight of the gas in question and divide by 22.4.

Example. To convert 400 ppm of methyl bromide (molecular weight 94.95 = 95 approximately)

400 ppm = 0.04% of volume = 0.4cm³ per litre

= 0.4×95 22.4= 1.7 g/m^3 (or mg/l or oz per l 000 ft³)

CONCENTRATION X TIME (c x t) PRODUCTS

Most fumigation treatments are recommended on the basis of a dosage given as the weight of chemical required for a certain space - expressed as grammes per cubic metre or pounds per 1000 cubic feet or as volume of liquid applied to a certain weight of material - expressed as litres per quintal or gallons per 1000 bushels. Usually, this designation of dosage is followed by a statement of the length of the treatment in hours

and the temperature or range of temperature at which the schedule will While such recommendations are usually based on treatments that apply. have proved successful under certain conditions, they should also take into account the fact that certain factors may modify the concentrations free to act against the insects. One important factor already mentioned is the effect of loads of different sizes (Figure 2). is the leakage from the structure undergoing treatment. What is really important is the amount of gas acting on the insects over a certain period of time. For instance, it is known (Bond and Monro, 1961) that in order to kill 99 percent of larvae of Tenebroides mauritanicus (L.) at a concentration of 33.2 milligrammes per litre of methyl bromide must be maintained for 5 hours. The product 33.2 milligrammes per litre x 5 hours = 166 milligrammes per litre x hours is known as the concentration x time product needed to obtain 99 percent control of this insect (Figure 4). It can be abbreviated and referred to as the c x t product. In the literature it is often expressed numerically with the notation mg h/l (milligramme hours per litre). In this example it would be known as the lethal dose for 99 percent of the population, or the LDgg.

In order to apply this method of treatment designation to practical fumigations, it is necessary to make reasonably correct determinations of the fumigant concentrations required to kill the insects under certain specific conditions; important modifying conditions are temperature and humidity. One such determination is illustrated graphically in Figure 4. Note that in this figure the concentration curve tends to flatten out for short exposures at high concentrations and long exposures at low concentrations and at these extremes, which are not likely to be employed in practice, the constant value for the c x t product does not hold. To illustrate specifically the use of the data in Figure 4, Table 3 sets out the required concentration x time products to bring about 99 percent mortality of $\underline{\mathbf{I}}$. $\underline{\mathbf{mauritanicus}}$ using methyl bromide at $20^{\circ}\mathrm{C}$ and 70 percent relative humidity for various exposures:

TABLE 3. - REQUIRED CONCENTRATION X TIME (c x t) PRODUCTS TO OBTAIN 97
PERCENT MORTALITY OF TENEBROIDES MAURITANICUS

| Concentration methyl bromide | Exposure | c x t product |
|---------------------------------|----------|---------------|
| mg/l | hours | mg h/1 |
| 83 | 2 | 166 |
| 55.3 | 3 | 166 |
| 41.5 | 4 | 166 |
| 33.2 | 5 | 166 |
| 23.7 | 7 | 166 |
| 16.6 | 10 | 166 |

It must be emphasized again that before they are applied in practical use each product must be calculated for the different stages of an insect species at a certain temperature and humidity. Under practical conditions, variations in temperature are particularly important. In practice, several insect species or stages of a given insect may be treated and therefore the c x t product required is that which is

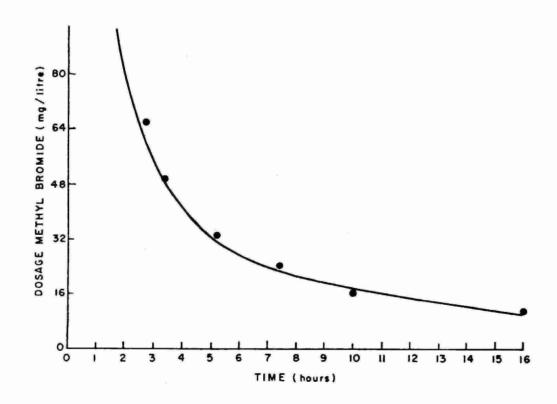


FIGURE 4. - Insect mortality and concentration x time products. A curve showing the relationship between concentration of methyl bromide and time of exposure against fourth instar larvae of $\underline{\text{Ic-ebroides}}$ mauritanicus for 99 percent mortality at 20°C . (Bond and Monro, 1961)

effective against the most tolerant species or stage present in the system.

The value and possible application of the c x t product for the fumigation of insects has been investigated by a number of workers (see particularly Whitney and Walkden, 1961; Harein and Krause, 1964; Estes, 1965; Bell and Glanville, 1973; Bell, 1977a, 1978). The important modifying effects of temperature, humidity and the moisture content of the commodity are emphasized. Kenaga (1961) described the use of graphs to estimate the effective use of c x t products of eight different fumigants against Tribolium confusum Duv. under varying conditions of time and temperature. Heseltine and Royce (1960) showed how integrated c x t products of ethylene oxide and methyl bromide may be used in practice with the aid of specifically designed concentration indicators in the form of sachets.

The use of integrated c x t products is particularly useful in routine fumigations when the reaction of a particular species or groups of species has been carefully worked out under the range of conditions likely to be encountered. It has been used successfully in large-scale eradication campaigns (Armitage, 1955; Monro, 1958c).

Figure 5 and Table 4 show how an integrated c x t product of methyl bromide may be applied in dealing with a specific problem. In this instance a hypothetical situation is illustrated in simplified form to show how the method could be applied under more complex conditions with multiple gas sampling points. The target of the fumigation is an insect which requires for complete control, under the prevailing conditions of temperature and humidity, a c x t product of 190 gramme hours per cubic metre $(g \ h/m^3)$, which is equivalent to 190 milligramme hours per litre $(mg \ h/l)$.

Leakage from the 100 m³ structure and sorption by the commodity are two factors that in this instance influence the concentration of fumigant in the free space and thus within the commodity. It is known that an initial dosage of 32 grammes per cubic metre (g/m^3) may bring about the desired conditions for this load of commodity in a 12-hour exposure period if the concentration in the free space is maintained above 20 milligrammes per litre (mg/l) during the entire exposure. This nominal dose is introduced and concentration readings are made at regular interusing a thermal conductivity analyser (see Chapter 4). Samples are vals taken from points in the free space and at the centre of the commodity then the data are plotted on a graph as shown in Fig. 5. At the beginning, particular attention is paid to the free space readings. After 2.5 hours it is clear that the free space concentration will fall below the stipulated 20 mg/l and 0.5 kg of fumigant are added to the system. Again, after a further 2.5 hours (total elapsed time 5 hours) another 0.5 kg are added to sustain the concentration. After 11.7 hours the desired c x t product of 190 g h/m3 has been attained and the treatment is terminated by initiating aeration. The integrated c x t product obtained within the commodity, calculated from the concentration plot, is arrived at as shown in Table 4.

Recommendations based on the c x t product principle provide a sound means of ensuring that the treatment is adequate to control the insects.

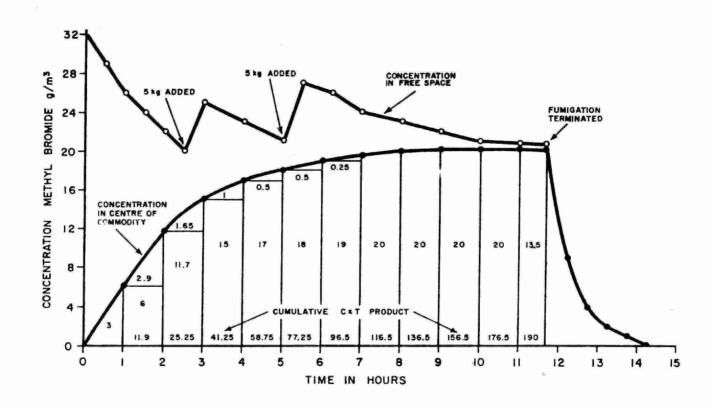


FIGURE 5. - Chart of progress of a fumigation with methyl bromide designed to achieve a cumulative c \times t product of 190 g h/m 3 .

TABLE 4. - INTEGRATED CONCENTRATION X TIME PRODUCTS WITHIN THE INFESTED COMMODITY

| Hours | Rectangle | Triangle | Total area | Cumulative |
|-------|-----------|----------|------------|------------|
| | | | | mg h/l |
| 1 | | 3 | 3 | 3 |
| 2 | 6 | 2.9 | 8.9 | 11.9 |
| 3 | 11.7 | 1.65 | 13.35 | 25.25 |
| 4 | 15 | 1 | 16 | 41.25 |
| 5 | 17 | 0.5 | 17.5 | 58.75 |
| 6 | 18 | 0.5 | 18.5 | 77.25 |
| 7 | 19 | 0.25 | 19.25 | 96.5 |
| 8 | 20 | - | 20 | 116.5 |
| 9 | 20 | = | 20 | 136.5 |
| 10 | 20 | - | 20 | 156.5 |
| 11 | 20 | - | 20 | 176.5 |
| 11.7 | 13.5 | - | 13.5 | 190.0 |

Dosage schedules are, perhaps, best given in terms of weight of chemical required for a certain space for a specified period of time along with the c x t products necessary to achieve control. Thus by monitoring gas concentrations during treatment, an applicator can add gas, extend the exposure or make other changes necessary to ensure success. For plant quarantine work, recommendations based on the c x t principle are particularly valuable because they promote uniformity in standards and permit reliable certification of goods so treated. Schedules based on these concepts are in use in several countries, e.g. Plant Protection and Quarantine Treatment Manual (USDA, 1976). For other treatments of stored products, where sorption in the commodity is appreciable, schedules based on the c x t principle but given in terms of weight of fumigant per unit volume of space and per unit weight of goods for specified exposure times have been worked out for some commodities (Thompson, 1970).

While the c x t method is useful for most fumigants, it cannot be employed with phosphine. Although concentration and exposure time are still the main factors that determine toxicity of this fumigant, the length of the exposure time is of great importance. Phosphine is a slow acting poison that is absorbed slowly by some insects even at high concentrations (Bond et al, 1969). Therefore, high concentrations may not increase toxicity; in fact, they may cause insects to go into a protective narcosis, as described later in this chapter. In a phosphine fumigation certain minimum concentrations are required, and therefore gas analysis should be carried out to ensure the presence of sufficient gas. For most treatments the manufacturers' directions will provide adequate treatment if no excessive loss through leakage or sorption occurs and adequate periods are allowed under gas.

Toxicity of Fumigants to Insects

As far as is known at present, fumigants enter the insect mainly by way of the respiratory system. The entrance to this system in larvae, pupae and adults is through the spiracles, which are situated on the lateral surfaces of the body. The opening and closing of the spiracles are under muscular control. To enter insect eggs, gases diffuse through the shell (chorion) of the egg or through specialized "respiratory channels". It has been shown that some gases may diffuse through the integument of insects, but at present the comparative importance of this route for the entry of fumigants is not known.

It is known that the poisoning of an insect by a fumigant is influenced by the rate of respiration of that insect; any factor that increases the rate of respiration tends to make the insect more susceptible.

The practical significance of the more important factors influencing the toxic action of fumigants is discussed in the following paragraphs.

EFFECT OF TEMPERATURE

General Effects

The most important environmental factor influencing the action of fumigants on insects is temperature. In the range of normal fumigating temperatures from 10 to 35°C, the concentration of a fumigant required to kill a given stage of an insect species decreases with the rise in temperature. From the purely biological standpoint, this is mainly due to the increased rate of respiration of the insects in response to the rise in temperature (Sun, 1946). Also, as pointed out previously, physical sorption of the fumigant by the material containing the insects is reduced and proportionately more fumigant is available to attack the insects. Therefore, within the range mentioned, conditions for successful fumigation improve as the temperature rises.

Low Temperature Fumigation

At below 10°C, the situation is more complicated. Below temperatures this point, increased sorption of the gas by the body of the insect may counterbalance the effects of decrease in respiration, and also the resistance of insects may be weakened by the effects of exposure to low temperatures. With some fumigants, less gas is required to kill certain species as the temperature is raised or lowered on either side of some point at which the insects are most tolerant (Moore, 1936; Peters and Ganter, 1935; Bond and Buckland, 1976). However, with others, toxicity to the insects declines as the temperature falls; for example, with methyl bromide there is a moderate decrease in toxicity down to the boiling point and below this temperature effectiveness drops off sharply that the amount of gas required to kill the insects increases dramatically, as shown in Figure 6.

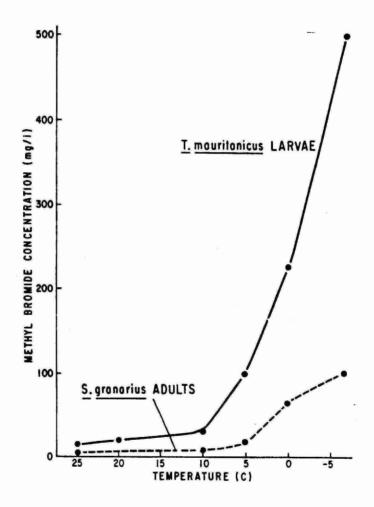


FIGURE 6. - Mortality (LD_{99}) of <u>Sitophilus granarius</u> adults and <u>Tenebroides mauritanicus</u> larvae when exposed to methyl bromide for eight hours at different temperatures.

For the reasons already given in the previous discussion, at lower temperatures sorption of the fumigant by the infested material is increased and more fumigant must be applied to compensate for this. Also, diffusion of a gas is slowed down in relation to reduction in temperature.

Prefumigation and Postfumigation Temperatures

It is important to bear in mind that the results of a fumigation may be influenced not only by the temperature prevailing during the treatment, but also by the temperatures at which the insects are kept before and after treatment.

If the insects have been kept in a cool environment, their metabolic rate will be low. If they are immediately fumigated at a higher temperature, their physiological activity may still be influenced by their previous history, and the uptake of the poison may not be as great as if they had been kept at the temperature of fumigation for a long time previous to treatment (Pradhan and Govindan, 1953-54). These phenomena can be of practical significance, particularly for certain species of insects that may go into a state known as diapause (see Howe (1962) for description of diapause and list of species involved). For insects in this state, tolerance to some fumigants, e.g. methyl bromide and phosphine, may be several times greater than for non-diapausing insects (Bell, 1977 a,b). For other species not in diapause, toxicity is usually found to be closely dependent on the temperature of the fumigation (Bond, 1975; Bond and Buckland, 1976).

A fumigator must have some knowledge of the previous history of the infested material as well as the species to be treated if he or she is to apply the recommended fumigation treatments most effectively. In all treatments, the material should be warmed to the treatment temperature for several hours to bring the insects to corresponding physiological activity before fumigating. If species disposed to the state of diapause are present (e.g. some members of the order Lepidoptera and the families Dermestidae and Ptinidae of the order Coleoptera) the dosage and exposure applied should be increased to a level that will kill the most tolerant insects.

Under experimental conditions, variations in postfumigation temperatures have been observed to influence insect mortalities, but the effects are more complex than those observed in the study of prefumigation temperatures. However, the net contribution of the postfumigation temperature effects would not be of sufficient importance in practice to influence the results of the procedures recommended in this manual. Reference to the papers of Sun (1946) and of Pradhan and Govindan (1953-54) should be made by those wishing to pursue this aspect of the subject.

Summary of Temperature Effects

From the foregoing discussion it is clear that temperature has farreaching effects on all the factors governing the successful outcome of fumigation. In order to clarify the significance of these effects they may be summarized as follows:

- For practical purposes, it is increasingly difficult to kill insects with fumigants as the temperature is lowered to 10°C. Below this point, in progression, various species or stages may succumb to low temperature or be weakened by it.
- Adsorption is the most important physical factor modifying the penetration of fumigants. The amount of gas physically adsorbed increases as the temperature is lowered, and it is necessary to add progressively more fumigant to sustain concentrations free to act on the insects. Furthermore, because of this inverse effect, at low temperatures diffusion of the gas into the material is slower during the treatment, and there is a corresponding decrease in the rate of desorption afterwards.
- 3. Chemical reaction of the fumigant with some of the fumigated material increases as the temperature is raised. If the residues formed are of significance, it is advisable to conduct the treatment at as low a temperature as possible, with due regard for the handicaps to successful results summarized in paragraphs (1) and (2).

In the light of these three main effects the influence of temperature in different types of fumigation may be considered:

- l. With commodities that are easily penetrated and are not highly sorptive, fumigation is practicable at relatively low temperatures with fumigants such as methyl bromide. It will be noted that some of the schedules of recommended treatments at the end of this manual include provision for fumigations at temperatures down to $4^{\circ}\mathrm{C}$.
- 2. Fumigation at temperatures at which the insects are not active may be advantageous in some quarantine treatments. There are two principal reasons for this. Firstly, if seeds or live plants in dormant condition are being fumigated, the risk of injury is reduced by avoiding the possible stimulating effects of higher temperatures on physiological mechanisms. Secondly, if the infesting insects are active fliers, their chances of escape from the material awaiting treatment in a cool environment are greatly reduced.
- With highly sorptive materials, on the other hand, low temperature fumigation may not be advisable because increased adsorption of the gas by the commodity may interfere with penetration. Also, under some conditions, the material may be hazardous for handling because the adsorbed fumigant is held longer at low temperatures.

EFFECT OF HUMIDITY

From the present knowledge of insect toxicology, it is not possible to make any general statements about the influence of humidity on the susceptibility of insects to fumigents. Variations in response at certain humidities have been observed not only between different species subjected to different fumigents but also between stages of the same species exposed to a single fumigent. However, variations due to humidity are not so important in practice as those due to temperature.

EFFECT OF CARBON DIOXIDE

Carbon dioxide, in certain concentrations, may stimulate the respiratory movements and opening of spiracles in insects. A number of authors have shown that addition of carbon dioxide to some of the fumigants may increase or accelerate the toxic effect of the gas (Cotton and Young, 1929; Jones, 1938; Kashi and Bond, 1975; Bond and Buckland, 1978). With each fumigant acting on different insects, there seems to be an optimum amount of carbon dioxide needed to provide the best insecticidal results. Excessive amounts of carbon dioxide tend to exclude oxygen from insects and thus interfere with the action of the fumigants.

With certain fumigants, such as ethylene oxide and methyl formate, the addition of carbon dioxide may work to advantage both by reducing the fire or explosion hazards and by increasing the susceptibility of the insects. On the other hand, with fumigants that are nonflammable, the advantages of adding carbon dioxide may be offset by the extra cost and work required to handle the additional weight of containers.

The use of carbon dioxide as a "fumigant" introduced artificially into grain storages or other structures is not registered for use in Canada.

PROTECTIVE NARCOSIS

Some fumigants can produce paralysing effects on insects that may alter the toxicity of these or other fumigants. In the use of hydrogen cyanide (HCN) against insects, it has been shown that, if certain species are exposed to sublethal concentrations before the full concentration is applied, the resulting fumigation is less effective than one in which the insects are subjected to the full concentration from the very beginning (Lindgren, 1938). A similar protective effect can also occur with the fumigant phosphine if insects are exposed to excessive concentrations during a treatment (Winks, 1974a). Also, insects that have been narcotized by sublethal concentrations of HCN have been found to be protected from lethal treatments with other fumigants, e.g. methyl bromide (Bond, 1961) and phosphine (Bond et al, 1969). This effect has been referred to as "protective stupefaction" or "narcosis".

Although phosphine itself can narcotize insects it does not, however, protect them from the action of methyl bromide as does HCN; in fact, phosphine and methyl bromide can be used together as a "mixture" to enhance the effectiveness of each other (Wohlgemuth et al, 1976; Bond, 1978).

From the practical point of view the phenomenon of narcosis is important because it can reduce the effectiveness of certain fumigants. However, steps can be taken to avoid problems of this nature:

 In fumigations with HCN the maximum concentration attainable from a recommended dosage should be achieved as soon as possible at the beginning of the treatment.

IIIVXX

- 2. HCN should not be applied with other fumigants such as methyl bromide or phosphine, if the maximum toxic effect is to be achieved.
- Excessive concentrations of phosphine likely to produce a protective narcosis should not be used.

FLUCTUATIONS IN SUSCEPTIBILITY OF INSECTS

It has often been observed that there may be fluctuations in the susceptibility of populations of insects to a given poison. Some of the reasons are known, while others need further clarification. Two important factors are undoubtedly seasonal changes in climate and the effect of nutrition. The susceptibility of insects may be greatly influenced by the quality of the food they consume. It also has been observed with some insects that a certain amount of starvation may make them more, rather than less, resistant to fumigants (Sun, 1946).

In practical work it is well to know that fluctuations in resistance may occur. The alert operator must always be on the lookout for any changed conditions that may necessitate modification of recommended treatments.

COMPARATIVE TOXICITY OF FUMIGANTS

Apart from the influence of the environment, there is a great variation in susceptibility of different species of insects to different fumigants. The successive stages of a given species may also vary greatly in response. Figure 7 illustrates this point. The data were obtained during an extensive study of the usefulness of HCN and methyl bromide for the disinfestation of empty ships (Monro et al, 1952).

Howe and Hole (1966) have shown that these variations in the susceptibility of stages of <u>Sitophilus granarius</u> (L.), observed under practical conditions, are closely confirmed in laboratory experiments.

A large number of studies have been made under laboratory conditions to determine the relative susceptibility of insects to different fumigants. Table 5 shows how fumigants may vary in their toxicity to common species. Bowley and Bell (1981) have reported on the toxicity of twelve fumigants to three species of mites infesting grain.

Acquired Resistance of Insects

Many species of insect have the ability to develop resistance to certain insecticides. With fumigants this problem of resistance is a matter of

TABLE .5. CONCENTRATION x TIME PRODUCTS* OF CERTAIN FUMIGANTS REQUIRED FOR THE CONTROL OF VARIOUS SPECIES OF INSECTS

| | Oryzaephilus surinamensis | Rhyzope rtha dominica | Sitophilus granarius | Sitophilus oryzae | Tenebroides mauritanicus | Tribolium confusum | Tribolium castaneum | T rogode ma g rana rium |
|------------------------------------|---|----------------------------|----------------------------|--------------------------------------|---|----------------------------|---|---|
| Fumigant | Adults **LD95 6 h 21 ^o C | Adults LD95 6 h 21°C | Adults LD99 5 h 25°C | Adults LD95 6 h 21°C | Larvae LD99 5 h 25 ^o C | Adults LD99 5 h 25°C | Adults LD90 6 h 24°C | Larvae LD95 8 h 21 ⁰ C |
| Ac rynonit rile | 48.4 | 48.4 | 111.0 | 410.8 | 140.0 | ¹ 19.5 | | 548.0 |
| Carbon disulphide | 4408.0 | 4294.0 | ¹ 325.0 | 4300.0 | ¹ 828.0 | ¹ 560.0 | | 5696.0 |
| Carbon tetrachloride | | | ¹⁰ 4 495.0 | ⁹ 2 220.0 | ¹ 2 400.0 (LD50) | 102 025.0 | 11600.0 | ~~~ |
| Chloropicrin | 419.2 | 415.6 | 1150.0 | 423.4 | ¹ 56.0 | ¹ 57.5 | 1114.0 | ⁵ 96.0 |
| Ethylene dibromide | 419.2 | 437.2 | 134.5 | 460.0 | ¹ 125.0 | 131.0 | ⁷ 22.0 (LD.95) 4 h 27°C | ⁵ 80.0 |
| Ethylene dichloride | 4462.0 | 4636.0 | ¹⁰ 1 230.0 | 4738.0 | 1 _{1 728.0} | 10365.0 | 11462.0 | 5 ₂ 080.5 |
| Ethylene oxide | 460.0 | 469.6 | 136.0 | 462.0 | ¹ 175.0 | ¹ 127.5 | ³ 135.0 (LD99) 5 h 25 ^o C | ⁵ 176.0 |
| Hydrogen cyanide (HCN) | 47.2 | 415.6 | ¹ 67.5 | ³ 60.0 (LD99) 5 h 25°C | ¹ 66.5 | ¹ 5.5 | ⁷ 2.4 (LD95) 4 h 27°C | ⁵ 26.4 |
| Methyl bromide | 440.8 | 433.0 | 128.0 | ² 30.0 (LD99.9) | ¹ 115.0 | 164.0 | ⁷ 62 0 (LD95) 4 h 27°C | ⁵ 136.0 |
| Phosphine (24 hr exposure 27°C) | ⁸ 0.96 (LD99) | 80.6 (LD99) | 81.01 | 8 _{0.36} (LD99) | ¹ 5.0 approx. | 80.48 | 1111.5 | 6331.0 100% mort. 72 h 21°C |
| Sulphuryl fluoride | | | ¹ 17.5 | | 181.5 | 155.0 | | |

^{*}In terms of milligramme hours per litre - **LD = Lethal dose - ¹Bond and Monro (1961) - ²Brown (1959) - ³Busvine (1938) - ¹Lindgren et al (1954) - ⁵Lindgren et al (1955) - ⁶Lindgren et al (1958) - ¹Lindgren and Vincent (1965) - ⁶Lindgren et al (1966) - ഐMajumitr (1962) - ¹OShepard et al (1937) - ¹¹Bang and Telford (1966).

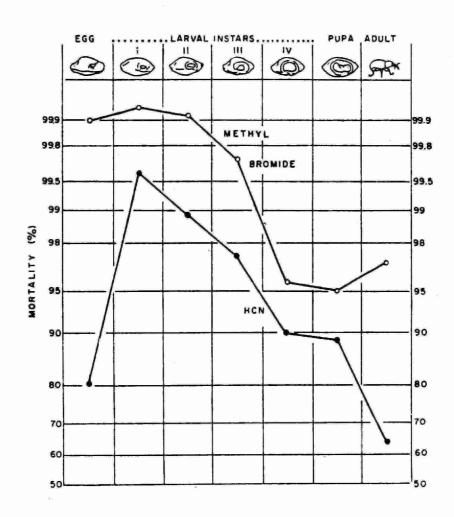


FIGURE 7. - The relative susceptibility of different life stages of Sitophilus granarius to HCN (dosage 0.72 to 0.84 percent by volume) and methyl bromide (0.21 to 0.76 percent by volume) during the fumigation of empty cargo ships. Exposure for 10 to 12 hours, temperature range 3 to 28°C.

(Monro et al, 1952)

increasing concern; in a global survey of stored grain pests, resistance to both of the major fumigants, phosphine and methyl bromide, was found in a number of insect species (Champ and Dyte, 1976). Collections of 849 strains of insects from 82 countries showed that 20 percent of the insects had some resistance to phosphine and 5 percent to methyl bromide. The highest level of resistance (10-12 times normal) was found in the lesser grain borer Rhyzopertha dominica (F.). It was concluded from this survey that resistance to fumigants was, as yet, limited in extent and often at marginal levels, but that it was of considerable significance as it posed a real threat to the future use of fumigants as control agents.

Research in laboratories has shown that a number of destructive stored product insects can develop appreciable resistance to fumigants. Selection of the granary weevil (Sitophilus granarius) has produced a strain with more than 12-fold resistance to methyl bromide (Bond and Upitis, 1976). A strain of the red flour beetle, Tribolium castaneum (Herbst), developed a 10-fold resistance to phosphine in six generations (Winks, 1974b).

There is recent evidence, from field studies in India and Bangladesh, of the development of resistance to phosphine in the Khapra beetle (Borah and Chalal, 1979) and other stored grain pests (Tyler et al, 1983).

Resistance to fumigants is of concern because of the great value of fumigants for pest control and because of the very limited number of materials available. Even low levels of resistance in species of insects that are cosmopolitan and easily transported to other parts of the world could be of serious consequence.

In view of the importance of resistance to fumigation, a brief and simplified account of some features of the problem are given below.

HOW RESISTANCE DEVELOPS

When a population of insects is exposed to an insecticide some individuals are killed more easily than others. The insects that are more difficult to kill may survive after the treatment and produce off-spring that are also hard to kill. These insects are said to be more tolerant because they can withstand above-average doses of the poison. If a population is repeatedly treated with the same insecticide and each new generation has increasingly higher tolerance, a "resistant" strain is produced. Resistance is a genetic characteristic that is passed on from one generation to the next.

In the laboratory, resistance is produced by treating a population to kill most of the insects, breeding the tolerant survivors to produce a new generation, re-treating and continuing the process until a resistant strain is obtained. This process is known as selection for resistance. A number of strains of insects with resistance to different fumigents have been produced in this way (Monro et al, 1972; Bond, 1973; Winks, 1974b; Bond and Upitis, 1976).

In the field, resistance to fumigants can develop in the same way. In a grain bin, on a cargo ship or any other place where a resident population of insects is treated over and over again with the same fumigant, resistance might develop. Insects that are not killed may produce new

generations with increasingly greater tolerance. Generally, resistance does not develop as readily in wild populations as in the laboratory because the selection process may be irregular and because they may interbreed with non-treated susceptible insects. However, the fact that resistance has been discovered in wild populations indicates the possibility that further resistance may develop where fumigants are used regularly.

NATURE OF RESISTANCE

Resistance is an inborn characteristic that allows individual insects to tolerate above average doses of a poison. Resistant insects usually are similar in appearance and have the same habits as susceptible insects. Normally, they can only be distinguished by their ability to tolerate excessive concentrations of the fumigant. Tests have been designed for detecting and measuring resistance to fumigants (FAO, 1975; UK, 1980).

An important feature in resistance is the ability to tolerate the effects of more than one poison. Insects that have resistance to one fumigant can, in some cases, also be resistant to other fumigants. This characteristic, known as "cross-resistance" is demonstrated by the data in Table 5. It can be seen that granary weevils selected with methyl bromide were also resistant to several other fumigants, and the levels of cross-resistance were all significant in terms of practical control. Such cross-resistance was not found, however, in insects selected with phosphine (Monro et al, 1972; Kem, 1978) or ethylene dibromide (Bond, 1973).

TABLE 5. - RESPONSE OF METHYL BROMIDE - RESISTANT GRANARY WEEVIL TO SIX OTHER FUMIGANTS*

| Fumigant | Resistant | Normal | Tolerance ratio |
|--------------------|-----------|--------|-----------------|
| Methyl bromide | 19.7 | 3.6 | 5.5 |
| HCN | 16.4 | 8.2 | 2.0 |
| Acrylonitrile | 4.9 | 1.05 | 4.7 |
| Ethylene oxide | 20.1 | 4.1 | 4.8 |
| Chloropicrin | 6.6 | 3.9 | 1.7 |
| Phosphine | 13.0 | 2.2 | 5.9 |
| Ethylene dibromide | 8.5 | 2.85 | 3.0 |

^{*} Dosage in mg/l for 5h, at 25°C required for 50 percent mortality (Monro et al, 1961).

TESTING FOR RESISTANCE (FAO, 1975)

For routine monitoring to detect the initial appearance of resistance in wild populations of stored product beetles, it is convenient to use a discriminating dose, which is expected to kill all susceptible specimens. The dose chosen is that corresponding to slightly above the LD99.9 obtained from the regression line for susceptible beetles allowing for, in the case of phosphine, what appears to be inherent variability of response. Some discriminating concentrations are given in Table 6. Susceptible reference strains must always be included in discriminating tests.

When using a discriminating test with fumigants it is always advisable to make provision for abnormal concentrations. If a concentration is obtained that is less than the discriminating concentration, this will be revealed by abnormal survival in the susceptible reference strain. Abnormally high concentrations may be revealed by the inclusion in the tests of a reference strain (or species) with slightly greater tolerance to the fumigant than the susceptible reference strain on which the discriminating dose is based, approximately x 1.5 for methyl bromide tests and x 2.5 for phosphine tests. An alternative approach is to use three dosages, one at the discriminating dose, one at the approximate LDgO level and the other at an equivalent level above the discriminating dose.

In regular monitoring for resistance, it should be detectable even when only a small proportion of resistant individuals is present. A minimum of 100 insects in two batches of 50 should be used per sample.

Limited numbers of insects may not be sufficient to detect low levels of resistance. Therefore, additional samples should be obtained, if possible. If, however, there is suspicion of serious resistance (e.g. from failure of treatments) a test with small numbers (10 to 20) may provide valuable early indication.

The insects are exposed to the discriminating dose for the appropriate period in the usual way. If all of them are dead at the end of the post-treatment holding period, the sample can be classified as "no resistance detectable", and the medium in which they were held is put into a hot-air oven to destroy the culture. On the other hand, the presence of surviving insects at the end of the test should be regarded as <u>primated</u> evidence of resistance and investigated further.

CONFIRMING RESISTANCE

The appearance of unaffected insects in a discriminating test could be due to the presence of unusually tolerant individuals from a normal population. Provided that the conditions of exposure, the physiological state of the insects and the dosages are consistent, the probability of a single insect in a batch of 100 being unaffected due to chance is less than 0.1 (e.g. less than once in 10 tests). It is important to determine whether incomplete response is due to such causes or to genuine resistance. This can be checked as follows:

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TABLE 6. - NORMAL SUSCEPTIBILITY DATA OBTAINED FOR METHYL BROMIDE AND PHOSPHINE, WITH DISCRIMINATING DOSAGES.

| | | LD99.9 | Discriminating dosage |
|--------------------------------|---------------|--------|--------------------------|
| | * * * * * * * | mg/1 | •••••••• |
| METHYL BROMIDE | | | |
| (Exposure period - 5 hours) | | | |
| Sitophilus oryzae (L.) | 3.6 | 4.8 | 6 |
| S. zeamais Motsch. | 3.2 | 5.4 | 6 |
| S. granarius (L.) | 5.1 | 7.5 | 9 |
| Rhyzopertha dominica (F.) | 4.0 | 7.4 | 7 |
| Tribolium castaneum (Herbst) | 8.4 | 11.7 | 12 |
| T. confusum Duv. | 8.6 | 11.2 | 13 |
| Oryzaephilus surinamensis (L.) | 5.8 | 8.5 | 9 |
| <pre>0. mercator (Fauv.)</pre> | 5.8 | 8.5 | 9 |
| | | | |
| | | | |
| | | | |
| PHOSPHINE | | | |
| | | | |
| (Exposure period - 20 hours) | | | |
| <u>Sitophilus oryzae</u> | 0.011 | 0.039 | 0.04 |
| S. zeamais | 0.007 | 0.013 | 0.04 |
| S. granarius | 0.013 | 0.041 | 0.07 |
| Rhyzopertha dominica | 0.008 | 0.028 | [™] 0.03 |
| Tribolium castaneum | 0.009 | 0.028 | 0.04 |
| T. confusum | 0.011 | 0.029 | 0.05 |
| Oryzaephilus surinamensis | 0.012 | 0.036 | 0.05 |
| O. mercator | 0.011 | 0.034 | 0.05 |

- 1. The test can be repeated using further samples from the same field population. The chances of adventitious failure to respond by a single individual in each of successive tests decline progressively (less than 0.01, 0.001, 0.0001 and so on). Survival of two or more indviduals throughout is even less likely. Therefore, the continued appearance of a proportion of unaffected individuals can be considered as proof of resistance.
- 2. Alternatively, the insects which were unaffected in the discriminating test may be kept and used for breeding a further generation. If their reaction is actually due to resistance, it will be found that a substantially larger proportion of their progeny will fail to respond to the discriminating dose.

When these tests indicate that a population of insects is resistant, then extensive testing should be carried out to determine the degree of resistance present.

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WAYS TO AVOID RESISTANCE

Precautions can be taken to reduce the possibility of insects developing resistance to fumigants.

Perhaps the most effective measure involves alternate control practices that do not require chemicals. Good sanitation procedures, proper storage conditions, insect resistant packaging and all other measures that prevent infestations from developing can do much to reduce the need for fumigants. Treatments such as aeration of the commodity, irradiation, temperature extremes, insect pathogens, etc. can also be employed.

Where fumigants have to be used on a regular basis, close guard should be kept against control failures. Complete control of all insects in a treatment is the best insurance against resistance.

Periodic checks for resistance should be made in areas that are fumigated regularly. If signs of resistance begin to appear (as indicated either by control failures or through the test procedure) then every effort should be made to eradicate the population. The measures necessary for eradication will vary in different situations; they may involve a number of procedures using both chemical and non-chemical means.

Rotation of fumigants may be effective in some instances, especially if cross-resistance is not a problem. For example, methyl bromide might be used at intervals in a control programme that relies mainly on phosphine.

One measure that is not advisable in dealing with resistance problems involves increased dosing. Such practices as doubling the dose of fumigant to achieve an economic level of control can magnify the problem unless complete eradication is assured. Any insects surviving increased doses may develop even higher levels of resistance than would occur with the normally recommended treatment.

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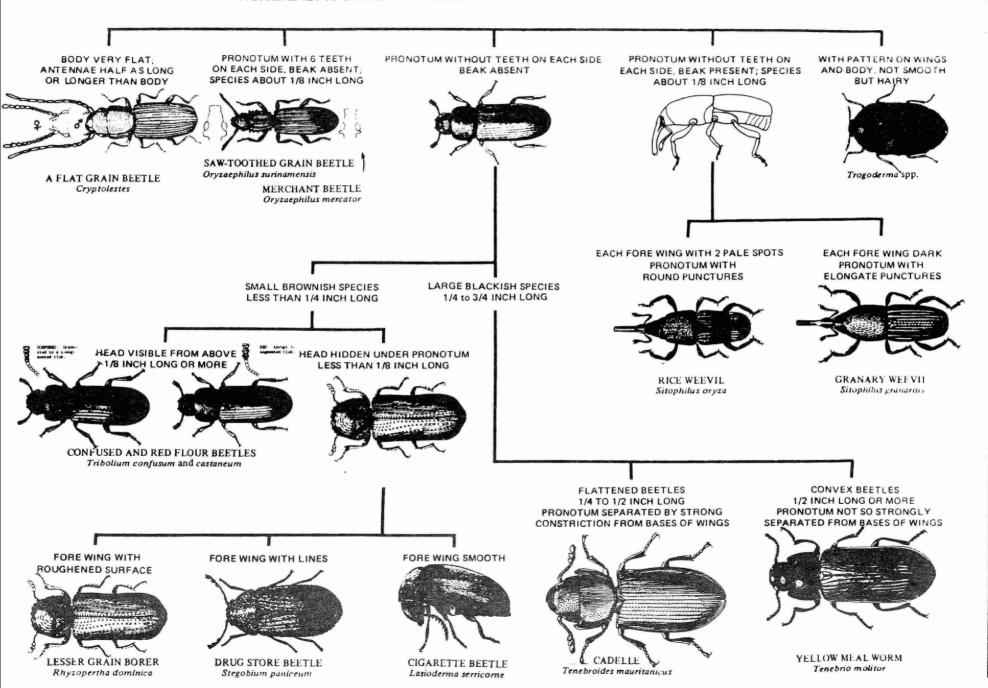
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INTRODUCTION

All pest control products containing methyl bromide are classified in Schedule 1 which, when used for a general space fumigation in the Province of Ontario, requires, under the <u>Pesticides Act</u> and Regulations, that the applicator be licensed appropriately and acquire a permit for use (Form 4).

Because it is colourless, practically odourless and tasteless, it is not apparent to the operator when a toxic atmosphere is encountered. As a result, some cases of methyl bromide poisoning have occurred from fumigation with methyl bromide.

The physical characteristics of methyl bromide make it especially adaptable for various types of fumigations. Space fumigation procedures are different from those used in soil fumigation. For further information on soil fumigation, consult the publication entitled "Methyl Bromide Soil Fumigation Procedures in Greenhouses".

PHYSICAL PROPERTIES OF METHYL BROMIDE

| Common Name | | Methyl Bromide (monobromomethane) |
|------------------------------------|------|---|
| Formula | • • | CH ₃ Br |
| Commercial Grades | | Not less than 99.5% pure. |
| Physical State | •. • | Gas at 20°C and 760 mm Hg. Liquid under pressure in cylinders or cans at 20°C. |
| Flash Point | | Practically nonflammable. Has been used as a fire extinguisher. |
| Boiling Point | • • | 3.6°C (38.5°F) at normal atmospheric pressure (760 mm Hg) |
| Colour | | Colourless. |
| Reaction with Metals | • | Not particularly corrosive to most metals. However, the liquid will react with aluminum, magnesium, and their alloys, possibly with ignition. |
| Odour | • | Odourless at fumigation concentrations. |
| Solubility | | Slightly soluble in water (1.34 $g/100 \text{ ml}$ at 25°C and 760 mm Hg). |
| Specific Gravity of Gas (Air = 1) | . , | . 3.27 at 0°C |
| Threshold Limit Value (Inhalation) | • | 5 ppm by volume (20 mg/m ³) (ACGIH - 1985) |

HAZARDS

Health Concerns

Methyl bromide is a very toxic chemical. Oral intake, vapour inhalation, or prolonged or repeated contact with the skin is harmful. Liquid contact with skin or mucous membranes can cause severe burns. Exposure to high concentrations of vapour may cause delayed skin burns. Vapour inhalation will cause lung irritation, varying from mild bronchitis to respiratory failure. The respiratory effects are usually accompanied or followed by effects on the central nervous system. The vapour has no appreciable odour in low concentrations. Concentrations above 1000 ppm have a sweet, chloroform-like odours. However, odour is not a reliable warning property.

The threshold limit value suggested by the American Conference of Governmental Industrial Hygienists (ACGIH) is 5 ppm in air by volume. (Time weighted average exposure which is safe for repeated daily exposures of 8 hours duration).

Acute Toxicity

Repeated exposures to 100 ppm, 7 hours a day, can produce very serious poisoning. Single exposures to 1000 ppm for 30 to 60 minutes are very dangerous to life. The effects are on both the respiratory and the central nervous systems. Unless the concentration is high enough to cause rapid narcosis and death from respiratory failure, the most striking response to exposure at high concentrations will be lung irritation resulting in congestion and oedema. Pulmonary effects may be somewhat delayed, and bronchial pneumonia often develops later. Symptoms may also include nausea and vomiting, cough, chest pain and shortness of breath. Central nervous system effects usually accompany,

or follow by several hours, the respiratory symptoms. Individuals exposed to lower concentrations may show only central nervous system effects. Their symptoms would include nausea and vomiting, dizziness, blurred vision, staggering gait and slurred speech. Convulsions are a common symptom.

At the first sign of any of the above symptoms, the affected person and his assistants should immediately get out of the fumigation area and into fresh air. Under some circumstances, symptoms may not show up until 48 hours after exposure.

The patient should be kept warm and the doctor called immediately. If the patient stops breathing, administer artificial respiration until a doctor arrives and takes charge. There is no antidote though treatments using sulfhydryl agents have been effective. The Fumigator should consult the Material Safety Data Sheets (copy is attached to this publication) and obtain further information from their supplier of methyl bromide gas.

First Aid

In case of accident, call a physician immediately. If there has been liquid contact with skin or clothing, remove all clothing and wash the skin with plenty of soap and water. If splashed into the eyes, flush the eyes with water for at least 15 minutes. If inhaled, place the patient in fresh air, face downward with head slightly below level of lungs. The patient should be kept warm. If the patient stops breathing administer artificial respiration until a doctor arrives and takes charge.

Chronic Toxicity

Exposure to low, but harmful, concentrations of methyl bromide over a long period of time, results in a variety of signs and symptoms, most of which are due to injury to the central nervous system. In order of frequency, these are: visual disturbances, slurred speech, numbness of the extremities, mental confusion, hallucinations, tremor and frequent fainting attacks. Symptoms may subside within a few days after termination of exposure, or may persist for several months. Numbness of the extremities and visual disturbances are the last to subside. Complete recovery is the rule.

Eyes

Direct contact of the eyes or eyelids to liquid methyl bromide may cause serious injury to either or both.

Skin

Since methyl bromide has a very low boiling point, it evaporates from the surface of the skin rapidly causing tingling, burning and numbness, followed by aching pain. However, if the material is spilled on clothing, gloves, or shoes, such coverings may maintain close and continuous contact of the methyl bromide with the skin. Since there is often no particular sensation produced by such contact, the individual may be unaware that the exposure has occurred, and burns may result. Blisters commonly appear after several hours. If exposure is not sufficient to cause blisters, itching dermatitis may appear after several days. Rubber gloves, jewellery, bandages, cigarettes, wallets, etc. should not be worn or carried when in an atmosphere containing methyl bromide.

METHYL BROMIDE AS A FUMIGANT

Methyl bromide is a very efficient space fumigant when handled and used according to label directions and accepted fumigation practices.

Methyl bromide has demonstrated its effectiveness on many species of insects and rodents. It kills insects in all stages of their life cycles through the spiracles of the respiratory system. Specialized respiratory channels or diffusion allows the fumigant to penetrate the egg. Since an increase in ambient temperature increases the rate at which an insect respires, it becomes more susceptible to the fumigant as the temperature rises.

Methyl bromide has the ability to penetrate almost any commodity quite readily and achieve a complete kill within 24 hours. Because temperature and other environmental conditions affect the dosage required to achieve a complete kill, the exposure may be shortened to a minimum of 8 hours if the dosage of methyl bromide is increased proportionally to the space under fumigation.

Depending on such factors as commodity temperature, fumigation seal and others, the degree of insect kill will vary. In some instances, delayed insect mortality may result at the end of a fumigation, or adults may be sterilized and moulting inhibited.

Types of Buildings that can be Fumigated with Methyl Bromide

Almost any frame or metal buildings that are in a sound condition (good repair and relatively air tight) can be fumigated. Some problems have been encountered with hollow or solid cement block walls because of their porous nature, however, they can be fumigated by increasing the dosage and the time of exposure.

Methyl bromide is registered for use in Canada for structural fumigation for the following uses, pests, and rates of application. Check the label for authorized uses.

| USE | PEST(S) | RATE OF APPLICATION |
|--|--|---|
| GRAIN (stored) - boxcar, warehouses, tarpaulin, vault, vacuum vault, mill (cereal and food) ship and bulk grain storage | | 3.25 - 6.50 kg/ 100 m ³ |
| CHEESE | - mites | 3.25 kg/100 m ³ (aerate for at least 48 hours) |
| FEED, FOOD, NONFOOD | | |
| - Dwellings, food -processing plants, tarpaulin, vault, vacuum vault trailer and space fumigation | all stored product insectsrodents | 2.50 - 3.25 kg/ 100 m ³ |
| | | |

NOTE:

In Ontario under the <u>Pesticides Act</u> and Regulation, a Structural Class 1 exterminator can use products containing methyl bromide only under the following conditions:

- the exterminator <u>must</u> be assisted by a Structural Class 1, 2 or 6 endorsed for methyl bromide structural licensed person at all times during the fumigation;
- a permit <u>is required</u> prior to the use of methyl bromide for a general space fumigation.

In Ontario, under the <u>Pesticides Act</u> and Regulation a Structural Class 6 exterminator endorsed for the use of methyl bromide can only use the product under the following conditions:

- the exterminator <u>must</u> be accompanied by a Structural Class 6 endorsed for methyl bromide or Structural Class 4 endorsed for methyl bromide licensed person at all times during the fumigation;
- 2. An endorsed licence is for a specific premise unless otherwise stated;
- 3. An endorsed Class 6 Structural Exterminator's licence for methyl bromide does <u>not</u> allow the licencee to use methyl bromide for space fumigation. Only tarpaulin, vault, vacuum vault, trailer and boxcar fumigations can be conducted. Permits are not required for these conditions if they meet the exemptions under the <u>Pesticides Act</u> (See 42, 43).
- 4. A person licenced as a Class 4 Structural exterminator, endorsed for methyl bromide may only use methyl bromide for tarpaulin, vault, vacuum, vault, trailer and boxcar fumigation and only in the presence of a Class 6 Structural Exterminator endorsed for use of methyl bromide.

ADVERSE EFFECT ON MISCELLANEOUS MATERIALS

The fumigation of some foodstuffs with methyl bromide may result in the creation of undesirable taints or odours. These may be transitory or permanent. In some instances they may be attributed to reactions with sulphur or sulphur compounds originally present or added during processing. Do not fumigate if the produce concerned will be damaged. If the moisture in grain is high or if the grain temperature is below 16°C, fumigation should not be carried out.

The following material foodstuffs should <u>not</u> be exposed to methyl bromide, or should be exposed only after conducting preliminary tests with small samples:

- iodized salt stabilized with sodium hyposulphite;
- salt blocks used for cattle licks;
- certain soap powders and baking sodas;
- sponge rubber;
- foam rubber as in rug padding, pillows, cushions and mattresses;
- rubber stamps and similar forms of reclaimed rubber;
- furs, horsehair and pillows (especially feather pillows);
- 8. leather goods, particularly white kid or any other leather goods tanned by a sulphur process;
- woollens, especially angora;
- 10. viscose rayons, made by a process that uses carbon disulphide;
- 11. cinder blocks or mixed concrete and cinder blocks (unless sealed);
- charcoal, which not only becomes contaminated but absorbs great amounts of methyl bromide and thus reduces effective fumigant concentrations;
- 13. paper that has been cured by a sulphide process and silver polishing paper;
- 14. photographic chemicals, not including cameras or films;
- 15. rug padding, vinyl, cellophane;
- 16. any other materials that may contain reactive sulphur compounds;
- 17. full fat soya flour.

Effect on Metal, Plastic and Rubber

Methyl bromide is a powerful solvent of organic materials, plastics and natural rubber. When pure it is non-corrosive to metals. Methyl bromide liquid reacts with aluminum in the absence of oxygen to form methyl aluminum bromide, which in the presence of oxygen ignites spontaneously with the development of intense heat.

PRECAUTION

Methyl bromide may react in the presence of a flame or glowing wire to form hydrobromic acid which may be corrosive or injurious to many materials, e.g., stainless steel.

Chlorpicrin in a mixture with methyl bromide has been known to cause some corrosion in steel cylinders, but no similar difficulties have occurred with other fumigation equipment. As a liquid, methyl bromide has a solvent action on many plastics and organic materials. Natural rubber is attacked and acquires a strong unpleasant smell. Synthetic rubber tubing (e.g., neoprene) should therefore be used instead of natural rubber when lengths of tubing have to be joined in preparing for a fumigation. The common plastics, polyethylene, polypropylene and polytetrafluoroethylene (PTFE) are only slightly affected by the liquid. At the concentrations used in fumigation, gaseous methyl bromide has little effect on plastic or rubber, and films or coated fabrics can be used for fumigation sheets.

GAS MASKS AND SELF-CONTAINED BREATHING APPARATUS

An approved full-face gas mask and canister or an approved selfcontained breathing apparatus should always be worn whenever there is any possibility of exposure to methyl bromide. Gas masks or self-contained breathing apparatus should be approved by the U.S. Bureau of Mines and/or the National Institute for Occupational Safety and Health (NIOSH) for use in methyl bromide atmosphere.

Before entering an atmosphere containing methyl bromide, be sure to check:

- (a) all gaskets for wear;
- (b) expiry date on canister;
- (c) for any cracks in the hose; and
- (d) the face mask for leaks.

To do this, put on the mask with the canister attached. Place a hand over the hole in the bottom of the canister and inhale. If perfectly tight, the face mask will collapse. Canister gas masks are only air purifying devices, it is therefore, essential that they are used only in atmospheres which contain sufficient oxygen to support life (more than 16% at sea level) and which contain generally no more than 2% concentration of methyl bromide by volume. If the concentration of methyl bromide by volume is suspected of being in excess of this limit, a self-contained breathing apparatus only should be used.

The operational life of a canister can vary from several minutes to an hour, depending on the design and/or the concentration to which it has been exposed. Once the canister becomes saturated with methyl bromide, it no longer protects the wearer. Consult the manufacturer for exact specifications.

A used canister should be broken and discarded for there is no sure way of determining the residual protection remaining in that canister.

PLANNING AND PREPARATION

Become fully acquainted with the building layout, volume, commodity to be fumigated, the fumigant properties, label restrictions and first aid procedures, and habits of the pest concerned.

- Know the general layout of the structure and all escape routes. Do not rely on old blueprints, as walls are often removed and new ones added.
- Consider the previous treatment history of any commodities present to determine tolerance levels and adverse effects the fumigant may have.
- Locate utility service connections and be familiar with locations of shut-offs and telephones.
- 4. Apply for a permit at least seven days prior to the fumigation from the Director as indicated under the Pesticides Act and Regulation. Attach a map showing the building to be fumigated and distance to nearby properties or points of impingement. Upon approval of a permit proceed to the next step.
- 5. Written notification must be received by local fire and police departments and the local Medical Officer of Health, of the chemical to be used, date and time of gas release, and date and time of aeration, at least 24 hours before the fumigation.
- 6. Inform every occupant of the building (or the owner or his representative) of the fumigation in writing, at least 24 hours before the fumigation.

- 7. Arrange all equipment and provide for standby equipment in the event of equipment failure.
- 9. Thoroughly seal all vents, roof vents (roof drains that lead rain water directly to the ground do not need to be sealed), drains, windows, doors, and other openings. Security guards must be posted at the final exit door during the fumigation preparation procedures and release period. All other doors must be posted and locked. Warning signs measuring 35 cm x 25 cm indicating "DANGER" in red letters at least 7 cm high on a white background indicating a fumigation is taking place and setting out the name of the fumigator and his emergency telephone number should be placed at each entrance. These signs must be illuminated at night.
- 10. Plan the ventilation of all treated areas well in advance.
- 11. Check the entire area to eliminate any open flames, switch off all motors and allow hot surfaces to cool.
- 12. Circulation is required by means of fans to ensure even gas distribution, because methyl bromide is heavier than air. One 40 cm fan is sufficient for every 1400 cubic metres. Place cylinders and fans in locations suitable to obtain maximum distribution of gas. Provision should be made to switch the fans off from outside the building.

Remove caps and crack valves of cylinders outside the building. Replace safety caps and valve caps prior to transport into the building.

Methyl bromide cylinders should be placed according to dosage requirements at strategic points throughout the structure. The valves should point in a direction such that the

fumigators do not cross the path of the released gas as they retreat toward the final exit, wearing approved respiratory equipment.

In large operations, or in structures with high ceilings or roofs, stand pipes or swirlers (curved copper tubing directed upward) are often attached to the cylinder outlets to distribute the gas to a greater height. In this technique, a short "T" is fitted to the top of the pipe to discharge the gas laterally and prevent contact with the ceiling. Liquid methyl bromide should not come directly in contact with painted surfaces.

- 13. Go through a simulated fumigation (dry run) first so that everyone knows his duties. Two properly licensed exterminators must work together at all times.
- 14. For a large fumigation, it would be helpful to mark arrows in chalk on floor to indicate direction and order of movements of the exterminators as gas is discharged.

Arrange the gas release procedure such that the exterminators are not in the building longer than 5-10 minutes from initial release of the gas and no longer than 30 minutes per 24 hour period.

- 15. Make a final check to clear all personnel. Call out loudly that a gas is being released to be sure all is clear.
- 16. Put on approved respiratory equipment. This apparatus should not be removed until the fumigators have reached the outside air and all the fumigant has been completely discharged.

- 17. Release the gas. During the course of the treatment, regular checks should be made for leakage of the fumigant outside the building. This is not only a necessary safety precaution but also will prevent failure of the fumigation due to a loss of the gas. Gas levels and temperature in the building should also be monitored throughout the fumigation. It is suggested that inside and outside monitoring be conducted at 30 minute intervals in the first hour followed by readings every 3 hours.
- 18. Aerate the building after the required contact period (usually 24 hours). Use wind direction to your advantage and be aware of poor air movement that may exist when an inversion occurs. When commencing aeration, both exterminators should put on approved respiratory apparatus (new canisters must be used). Open as many doors and windows as possible from the outside. Start ventilators and Leave the immediate vicinity for approximately 30 Then with approved respiratory apparatus on, enter the building to open doors and windows. Enter the building for short periods of time only, then withdraw into fresh air upwind, remove the respirator for about 15 minutes then put it on again and re-enter the structure to open more windows. Allow at least one hour to aerate. At the end of this period, the halide leak detector will then indicate areas requiring additional aeration. Check at the floor level in corners, closets, store rooms, basement areas where methyl bromide may accumulate, as well as the main open areas. the use of an open flame in a grain mill is prohibited by law; use gas detector tubes, thermal conductivity units, automatic halogenleak TIF units, infrared analyzers or photovac units instead.
- 19. When the fumigators have determined that the building has been properly aired, tests for any residual fumigant must be carried out. Some materials, such as flours, grain meals and jute bags retain gas. This retention may be prolonged by introducing cold air into a building that was warm during the fumigation. In this case, the building must be reheated and tested for any residue.

20. Notify the Ministry of the Environment in writing, within 7 days that the fumigation has been completed.

TARPAULIN FUMIGATION

The use of plastic sheets or tarpaulins for fumigation is both cost effective and practical. An area is designated, as outlined in Section 42 and 43 of the Pesticides Act and Regulations

which can be isolated from work activity and can be safely aerated. Only clear polyethylene gas proof tarpaulins should be used since very often the fumigator needs to climb on top of the stack to assure proper tarp coverage. Stacked commodities or cargo should be on airtight surfaces (not asphalt). Place or rearrange several sacks or bags of material on top of the stack (place in the centre and corners) to form a gas expansion area enabling better distribution of the methyl bromide and to prevent the tarp from ripping on sharp corners.

An evaporation pan (place several stones in the pan for weight) should be placed on the top of the stack. Affix polyethylene hosing from the pan or bucket to the gas cylinder. Make a small hole in the tarp and seal around the hose entry point with masking tape. The tarp can be sealed to the floor by using sand snakes or masking tape. Sweep the floor surface prior to sealing. Provide a 60 cm to 100 cm overlap.

A jiffy applicator can be used to release the gas from 0.454 kg cans. A full face gas mask and approved canister must be worn by both the fumigator and the assistant.

A tarped stack should be posted with a warning sign and left undisturbed for the required exposure period (usually 24 hours). Check for leaks with a gas leak monitor.

Aeration should take place with all doors open and as much cross-ventilation as possible (fans can be used for this purpose). Standing upwind and wearing approved respiratory equipment,

partially pull the tarp off the stack and let it aerate for at least 30 minutes. Make certain no personnel are in the immediate vicinity, especially downwind. After this period of time, pull the tarp completely off the stack. Aerate the tarp fully, prior to storage.

USE OF THE HALIDE GAS DETECTOR

- After releasing the gas, check from the outside, the first floor and basement doors, windows and other openings for excessive leakage. Seal any substantial leaks.
- 2. Check the concentration of gas when aeration of the building begins. This check indicates the approximate amount of gas to which the exterminators will be exposed during aeration. It will also give an approximate indication of the loss of the fumigant during the fumigation. This information is helpful in determining the dosage to use in future fumigations of the building.
- 3. During aeration, rest periods should be taken by the exterminators. The rest stations should be a considerable distance upwind from the building under fumigation and in an area free from gas. It is always advisable to check with the gas detector to be sure no gas is present.
- 4. Use the gas detector to determine when the building is completely aerated and safe to be turned back to the owner for re-entry by the workmen.

DETERMINATION OF METHYL BROMIDE GAS

The Halide Leak Detector is an inexpensive and moderately accurate means of determining the absence or presence of harmful

concentrations of methyl bromide gas. This detector operates with acetylene, propane, kerosene or methyl alcohol fuel. In air containing methyl bromide, the flame will react to the various gas concentrations carried through the copper ring and across the flame. A long rubber hose acts as a suction tube to bring the air/gas mixture to the flame. Other halide gases (e.g. Freon) will also react with this detector.

The following table gives the approximate methyl bromide concentration associated with colour intensity in the flame.

| Methyl Bromide Present in ppm | Reaction of Flame |
|---------------------------------------|---|
| 0 10 | Very light blue Very faint green tinge at edge of flame |
| 20 30 100 200 500 1000 | Light green edge to flame Light green flame Moderate green Intense green, blue at edge Blue green Intense blue |

If the gas is detectable with your halide leak detector, it is not safe for any person to be in the area without approved breathing apparatus. Note: Persons who are slightly blue/green colour blind will not see any difference in the flame colour between 0 and 20 ppm. Detection tube should be used instead.

Gas detector tubes are available from safety supply companies. Readings are taken by breaking the two tips of the reaction tubes such that the air/gas mixture can be drawn through the tube. The

number of strokes required (i.e. number of pumps) to draw the air/gas through the pump is given on the tube (e.g. n=4 refers to 4 strokes). When a long hose line is used to monitor gas in the building from the outside, the line must be purged to obtain accurate readings. The fumigator should become familiar with the operating instructions supplied by the manufacturers of the various detector tubes.

Thermal conductivity units are among the most accurate of the fumigant monitors at moderate to high concentration. However, they require frequent recalibration. Their operation is based on two air chambers, one containing a verified gas standard and the other the air/gas sample to be monitored. A wire running through both chambers is electrically charged such that the constant current is affected by the final temperature (at equilibrium) of the wire and the difference of the resistance of the gases in the two chambers. This difference in resistance is measured on a built-in galvanometer.

Infra-red analyzers are the most expensive and most accurate of the gas monitors. Other gas monitoring equipment includes portable gas chromatography units, the Volhard titration method, and interference refractometers. Prices and degrees of sensitivity of these units vary considerably.

For a complete review of up-to-date fumigation procedures, consult the "Manual of Fumigation for Insect Control". FAO Plant Production and Protection Paper 54 by Dr. E. Bond. The products containing methyl bromide and listed below are currently registered and scheduled for use in Ontario. It is suggested you contact these companies for up-to-date information and safety guide booklets for the proper use of their products.

| PCP # | SCHEDULE | PRODUCT NAME | CANADIAN AGENT ADDRESS |
|-------|----------|---|---|
| 8790 | 1 | METHYL BROMIDE THE PENETRATING FUMIGANT | The Pestroy Co. Ltd. 1655 Edouard-Laurin Blvd. St. Laurent, Montreal Quebec H4L 2V6 |
| 9564* | 1 | METHO-O-GAS | Ciba-Geigy Canada Ltd. Agricultural Division 6860 Century Avenue Mississauga, Ontario L5N 2W5 |
| 9565* | 1. | BROMO-O-GAS | as above |
| 9566* | 1 | BROMO-O-GAS | as above |
| 12088 | 1 | PFIZER METHYL BROMIDE FUMIGANT | Pfizer Chemicals and Genetics Ltd. Box 2005 1 Wilton Grove Road London, Ontario N6A 4L6 |
| 12091 | 1 | PFIZER METHYL BROMIDE TOBACCO PLANT BED FUMIGANT | as above |

^{*} Registrant is: Great Lakes Chemical Corp.

P.O. Box 2200 West Lafayette

Indiana, U.S.A. 47906

(317) 463-2071

| 12326 | 1 | SANEX MB-C2 | Sanex Chemicals Ltd. 2695 Slough St. Mississauga, Ontario L4T 1G2 |
|---------|---|-----------------------------------|---|
| 12248 | 1 | GARDEX METHYL BROMIDE FUMIGANT | Gardex Chemicals Ltd. 246 Attwell Drive Rexdale, Ontario M9W 5B4 |
| 13477* | 1 | TERR-O-GAS 67 | Ciba-Geigy Canada Ltd. Agricultural Division 6860 Century Avenue Mississauga, Ontario L5N 2W5 |
| 16495** | 1 | METHYL BROMIDE FUMIGANT | Sanex Chemical Ltd. 2695 Slough Street Mississauga, Ontario L4T 1G2 |

** Registrant is: Americo Laboratories

7330 St. Hubert Rue

Montreal, Quebec

H2R 2N3

Parent U.S. Distributor: Ameribrom Inc.

1250 Broadway

New York, N.Y. 10001

(212) 563-4600



MOL 1219 (03/88)

Ministry of the Environment

Ministèro

Hazardous Contaminants Coordination Branch

Direction de la coordination des normes sur les polluents dangereux

do l'Environnement

The Pesticides Act - Form 4 Application for a Permit to Use a Pesticide Containing Methyl Bromide, or Phosphide or Cyanide Compounds

La loi sur les pesticides - formule 4 Demande de permis d'utilisation d'un pesticide contenant du bromure de méthyle, des

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MATERIAL SAFETY DATA SHEET

-----CANUTEC is the Canadian Transport Emergency Centre (in French, Centre canadien d'urgence transport). The Centre, a public service, is located in Ottawa and is operated by the Transport of Dangerous Goods Branch of Transport Canada.

CANUTEC provides immediate advice to those who need or request help in case of an emergency situation involving dangerous goods resulting in a spill, leak, fire or human exposure.

CANUTEC operates 24 hours a day, seven days a week, including holidays.

Call CANUTEC collect (613) 996-6666.

SPILLS ACTION CENTRE

The Ministry of the Environment's Spills Action Centre receives notification of spills 24 hours per day, 365 days per year on a province-wide toll-free number 1-800-268-6060 SUBSTANCE IDENTIFICATION

CAS-NUMBER 74-83-9

SUBSTANCE: METHYL BROMIDE

TRADE NAMES/SYNONYMS:

BRONOMETHANE; MBX; METHYL BROMIDE, LIQUID; METHOGAS; ROTOX; BROMOGAS; CELFUME; DOW FUME; DOWFUME MC-2; METAFUME; EMBAFUME; ISCOBROME; PESTMASTER; PROFUME; TERR-O-GAS 100; ZYTOX; HALON 1001; MONOBROMOMETHANE; U029; UN 1062; - OHS14300

CHEMICAL FAMILY:

HALOGEN COMPOUND, ALIPHATIC

MOLECULAR FORMULA: C-H3-BR

MOL WT: 95

CERCLA RATINGS (SCALE 0-3): HEALTH=3 FIRE=1 REACTIVITY=0 PERSISTENCE=1

NFPA RATINGS (SCALE 0-4): HEALTH=3 FIRE=1 REACTIVITY=0

COMPONENTS AND CONTAMINANTS

COMPONENT: METHYL BROMIDE

PERCENT: 100

OTHER CONTAMINANTS: NONE

--- EXPOSURE LIMITS:

METHYL BROMIDE:

20 PPM OSHA CEILING (CKIN) 5 PPM ACGIH TWA (SKIN)

LOWEST FEASIBLE LIMIT NIOSH RECOMMENDED EXPOSURE CRITERIA

1000 POUNDS SARA SECTION 302 THRESHOLD PLANNING QUANTITY 1000 POUNDS SARA SECTION 304 REPORTABLE QUANTITY

PHYSICAL DATA

DESCRIPTION: COLORLESS, TRANSPARENT, GAS OR VOLATILE LIQUID WITH A BURNING

TASTE, AND CHLOROFORM-LIKE ODOR.

BOILING POINT: 38 F (4 C)

MELTING POINT: -135 F (-93 C) SPECIFIC GRAVITY: 1.7 6 0 C

VAPOR PRESSURE: 1250 MMHG @ 20 C SOLUBILITY IN WATER: 1.75% @ 20 C

VAPOR DENSITY: 3.3

SOLVENT SOLUBILITY: ALCOHOL, CHLOROFORM, ETHER. BENZENE, CARBON DISULFIDE. CARBON TETRACHLORIDE

FIRE AND EXPLOSION DATA

FIRE AND EXPLOSION HAZARD: SLIGHT FIRE HAZARD WHEN EXPOSED TO HEAT OR FLAME.

UPPER EXPLOSIVE LIMIT: 16% LONER EXPLOSIVE LIMIT: 10%

AUTOIGNITION TEMP.: 1000 F (538 C)

FIREFIGHTING MEDIA:
DRY CHEMICAL, CARBON DIOXIDE, WATER SPRAY OR FOAM
(1984 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.3).

FOR LARGER FIRES, USE WATER SPRAY, FOG OR FOAM (1984 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.3).

FIREFIGHTING:

MOVE CONTAINERS FROM FIRE AREA IF POSSIBLE. FIGHT FIRE FROM MAXIMUM DISTANCE. DIKE FIRE CONTROL WATER FOR LATER DISPOSAL. DO NOT SCATTER MATERIAL (1984 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.3, GUIDE PAGE 55).

USE AGENTS SUITABLE FOR TYPE OF FIRE. USE WATER IN FLOODING AMOUNTS AS FOG. COOL CONTAINERS WITH FLOODING AMOUNTS OF WATER, APPLY FROM AS FAR A DISTANCE AS POSSIBLE. AVOID BREATHING POISONOUS VAPORS, KEEP UPWIND. EVACUATE DOWNWIND FOR LEAKS.

FIRE FIGHTING PHASES: USE NATER SPRAY, FOAM, CARBON DIOXIDE, OR DRY CHEMICAL. DO NOT WALK INTO SPILLS OF LIQUID OR ENTER HIGH CONCENTRATIONS OF VAPORS (NFPA 49, HAZARDOUS CHEMICALS DATA, 1975).

TRANSPORTATION DATA

DEPARTMENT OF TRANSPORTATION HAZARD CLASSIFICATION 49CFR172.101: POISON B

DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS 49CFR172.101 AND 172.402: POISON

TOXICITY

METHYL BROMIDE:

KIDNEYS.

60,000 PPM/2 HOURS INHALATION-MAN LCLO; 1 GM/M3/2 HOURS INHALATION-CHILD LCLO; 35 PPM INHALATION-HUMAN TCLO; 214 MG/KG ORAL-RAT LD50; 302 PPM/8 HOURS INHALATION-RAT LC50; 1540 MG/M3/2 HOURS INHALATION-HOUSE LC50; 2000 MG/M3/11 HOURS INHALATION-RABBIT LCLO; 300 PPM/9 HOURS INHALATION-GUINEA PIG LCLO; MUTAGENIC DATA (RTEC); CARCINOGEN STATUS: NONE. METHYL BROWIDE IS TOXIC, AND A SKIN IRRITANT, CENTRAL NERVOUS SYSTEM DEPRESSANT, CONVULSANT, AND NEUROTOXIN. POISONING MAY AFFECT THE BRAIN AND

HEALTH EFFECTS AND FIRST AID

OHS14300 PAGE 03 OF 06

INHALATION:

METHYL BROWIDE:

NARCOTIC/NEUROTOXIN/CONVULSANT/TOXIC.

2000 PPM IMMEDIATELY DANGEROUS TO LIFE OR HEALTH.

ACUTE EXPOSURE- SYMPTOMS MAY BE DELAYED FROM 1-4 HOURS AND MAY INCLUDE HEADACHE, VISUAL DISTURBANCES, NAUSEA, VOMITING, WEAKNESS, MALAISE, VERTIGO, PARESTHESIAS AND PARALYSIS OF THE EXTREMITIES, OLIGURIA OR ANURIA, DROWSINESS, CONFUSION, HYPERACTIVITY, HYPOTENSION, MENTAL CONFUSION, MANIA, TREMORS, UNSTEADY GAIT, AND EPILEPTIFORM CONVULSIONS. HIGH CONCENTRATIONS MAY CAUSE RAPID NARCOSIS AND DEATH FROM RESPIRATORY FAILURE. LESSER CONCENTRATIONS MAY CAUSE PULMONARY IRRITATION, CONGESTION, AND EDEMA AND DEVELOP TO BRONCHIAL PNEUMONIA. DEATH MAY ALSO RESULT FROM COMA, RESPIRATORY AND CIRCULATORY COLLAPSE. TUBULAR DAMAGE IN THE KIDNEYS HAS BEEN OBSERVED IN FATAL CASES. BOTH CENTRAL AND PERIPHERAL NEUROLOGIC DEFICITS MAY PERSIST AFTER POISONING INCLUDING VERTIGO, DEPRESSION, HALLUCINATIONS, ANXIETY AND INABILITY TO CONCENTRATE.

CHRONIC EXPOSURE- REPEATED EXPOSURE MAY RESULT IN ADVERSE CENTRAL NERVOUS SYSTEM EFFECTS INCLUDING LETHARGY, MUSCULAR PAINS, VISUAL, SPEECH, AND SENSORY DISTURBANCES, MENTAL CONFUSION, BLURRED VISION, PAPILLEDEMA, HALLUCINATIONS, SOMNOLENCE, FAINTING ATTACKS, BRONCHOSPASMS, AND CENTRAL NERVOUS SYSTEM EDEMA. PERIPHERAL NEUROPATHY MAY BE INDICATED BY PARALYSIS OF THE EXTREMITIES, MYOCLONUS, POLYNEURITIS, AND CONVULSIONS. LIVER AND KIDNEY DAMAGE MAY OCCUR.

FIRST AID: REMOVE FROM EXPOSURE AREA TO FRESH AIR IMMEDIATELY. IF BREATHING HAS STOPPED, GIVE ARTIFICIAL RESPIRATION. MAINTAIN AIRWAY AND BLOOD PRESSURE AND ADMINISTER OXYGEN IF AVAILABLE. KEEP AFFECTED PERSON WARM AND AI REST. ADMINISTRATION OF OXYGEN SHOULD BE PERFORMED BY QUALIFIED PERSONNEL. GET MEDICAL ATTENTION IMMEDIATELY.

SKIN CONTACT:

METHYL BROMIDE:

IRRITANT/NEUROTOXIN/CONVULSANT.

ACUTE EXPOSURE- CONTACT WITH THE LIQUID MAY CAUSE IRRITATION, SCALING, AND ITCHING DERMATITIS, AND FROSTBITE. THE LIQUID MAY BE ABSORBED TO CAUSE MAUSEA, VOMITING, BLURRED VISION, VERTIGO, WEAKNESS, PARALYSIS, OLIGURIA OR ANURIA, DRONSINESS, CONFUSION, HYPERACTIVITY, HYPOTENSION, COMA, AND CONVULSIONS WHICH DEVELOP OVER A LATENT PERIOD.

CHRONIC EXPOSURE- REPEATED OR PROLONGED EXPOSURE MAY LEAD TO VESICULATION, ERYTHEMA, AND EDEMA OF THE SURROUNDING SKIN. SYSTEMIC EFFECTS MAY INCLUDE BLURRED VISION, PAPILLEDEMA, NUMBNESS OF THE EXTREMITIES, CONFUSION, HALLUCINATIONS, SOMNOLENCE, FAINTING ATTACKS, AND BRONCHOSPASMS.

FIRST AID-REMOVE CONTAMINATED CLOTHING AND SHOES IMMEDIATELY. WASH AFFESTED AREA HITH SOAP OR MILD DETERGENT AND LARGE AMOUNTS OF WATER UNTIL NO EVIDENCE OF CHEMICAL REMAINS (AT LEAST 15-20 MINUTES). IN CASE OF CHEMICAL BURNS, COVER AREA WITH STERILE, DRY DRESSING. BANDAGE SECURELY, BUT NOT 100 TIGHTLY. GET MEDICAL ATTENTION IMMEDIATELY.

EYE CONTACT:

METHYL BRUMIDE:

ACUTE EXPOSURE- VAPORS AND LIQUID MAY CAUSE TRANSIENT IRRITATION AND CONJUNCTIVITIS. SYSTEMIC OCULAR EFFECTS FROM INHALATION OF SKIN CONTACT MAY RECULT IN BLURKEE OF CHMET COLUMN, DIFFULIA, AND TEMPORARY FIRMSESS.

EXPERIMENTAL APPLICATION OF A VERY SEVERE EXPOSURE TO PARRIT FYES RESULTED IN REVERSIBLE DAMAGE INCLUDING CONJUNCTIVITIS, FDFMA, STROMAL OPACITY, AND LOSS OF CORNEAL EPITHELIUM.

CHRONIC EXPOSURE- REPEATED OR PROLONGED EXPOSURE MAY CAUSE CONJUNCTIVITIS.

FIRST AID- WASH EYES IMMEDIATELY WITH LARGE AMOUNTS OF WATER, OCCASIONALLY LIFTING UPPER AND LOWER LIDS, UNTIL NO EVIDENCE OF CHEMICAL REMAINS (AT LEAST 15-20 MINUTES). IN CASE OF BURNS, APPLY STERILE BANDAGES LOOSELY WITHOUT MEDICATION. GET MEDICAL ATTENTION IMMEDIATELY.

INGESTION:

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METHYL BROWIDE:

ACUTE EXPOSURE- NOT APPLICABLE (GAS).

CHRONIC EXPOSURE- REPEATED ADMINISTRATION BY ORAL GAVAGE AS A SOLUTION IN ARACHIS DIL INDUCED TUMORS OF THE FORESTOMACH.

REACTIVITY

REACTIVITY:

- STABLE UNDER NORMAL TEMPERATURES AND PRESSURES.

INCOMPATIBILITIES:

METHYL BROMIDE:

ALUMINUM: SEVERE EXPLOSION HAZARD.

MAGNESIUM: SEVERE EXPLOSION HAZARD.

ZINC: SEVERE EXPLOSION HAZARD.

DIMETHYL SULFOXIDE: DELAYED EXPLOSION HAZARD.

STRONG OXIDIZERS: VIGOROUS REACTION. ETHYLENE OXIDE: VIGOROUS REACTION.

DECOMPOSITION:

THERMAL DECOMPOSITION MAY RELEASE CORROSIVE FUMES OF BROMIDE.

POLYMERIZATION:

HAZARDOUS POLYMERIZATION HAS NOT BEEN REPORTED TO OCCUR UNDER NORMAL TEMPERATURES AND PRESSURES.

STORAGE AND DISPOSAL

STORAGE: PROTECT AGAINST PHYSICAL DAHAGE. STORE ONE-POUND CONTAINERS IN DRY LOCATION TO PREVENT RUSTING. OUTSIDE OR DETACHED STORAGE IS PREFERRED FOR CYLINDERS. STORE IN WELL-VENTILATED LOCATION OUT OF THE DIRECT RAYS OF THE SUN AND PROTECTED FROM SNOW AND ICE (NFPA 49, HAZARDOUS CHEMICALS DATA, 1975).

CONDITIONS TO AVOID

MAY BURN BUT DOES NOT IGNITE READILY. CONTAINERS MAY EXPLODE IN HEAT OF FIRE.

METHYL BROWIDE:

IT WILL BURN IN AIR IN THE PRESENCE OF A HIGH ENERGY SOURCE OF IGNITION AND WHEN WITHIN A NARROW FLAMMABILITY RANGE.

SPILL AND LEAK PROCEDURES

OCCUPATIONAL SPILL:

DO NOT TOUCH SPILLED MATERIAL. STOP LEAK IF YOU CAN DO IT WITHOUT RISK. USE WATER SPRAY TO REDUCE VAPORS. FOR SMALL SPILLS, TAKE UP WITH SAND OR OTHER ABSORBENT MATERIAL AND PLACE INTO CONTAINERS FOR LATER DISPOSAL. FOR SMALL DRY SPILLS, WITH A CLEAN SHOVEL PLACE MATERIAL INTO CLEAN, DRY CONTAINERS AND COVER. HOVE CONTAINERS FROM SPILL AREA. FOR LARGER SPILLS, DIKE FAR AHEAD OF SPILL FOR LATER DISPOSAL. KEEP UNNECESSARY PEOPLE AWAY. ISOLATE HAZARD AREA AND DENY ENTRY. VENTILATE CLOSED SPACES BEFORE ENTERING. If a spill occurs, the Spills Action Centre of the Ministry of the Environment, must be notified immediately by calling 1-800-268-6060.

PROTECTIVE EQUIPMENT

VENTILATION:

PROVIDE LOCAL EXHAUST OR PROCESS ENCLOSURE VENTILATION TO HEET PUBLISHED EXPOSURE LIMITS.

RESPIRATOR:

THE FOLLOWING RESPIRATORS AND MAXIMUM USE CONCENTRATIONS ARE RECOMMENDATIONS BY THE U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, MIOSH POCKET GUIDE TO CHEMICAL HAZARDS OR NIOSH CRITERIA DOCUMENTS; OR DEPARTMENT OF LABOR, 29CFR1910 SUBPART Z.

THE SPECIFIC RESPIRATOR SELECTED MUST BE BASED ON CONTAMINATION LEVELS FOUND IN THE WORK PLACE AND BE JOINTLY APPROVED BY THE NATIONAL INSTITUTE OF OCCUPATIONAL SAFETY AND HEALTH AND THE MINE SAFETY AND HEALTH ADMINISTRATION.

AT ANY DETECTABLE CONCENTRATION:

SELF-CONTAINED BREATHING APPARATUS WITH FULL FACEPIECE OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE.

SUPPLIED-AIR RESPIRATOR WITH FULL FACEPIECE OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE IN COMBINATION WITH AN AUXILIARY SELF-CONTAINED BREATHING APPARATUS OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE.

ESCAPE- AIR-PURIFYING FULL FACEPIECE RESPIRATOR (GAS MASK) WITH A CHIN-STYLE OR FRONT- OR BACK-MOUNTED ORGANIC VAPOR CANISTER.

ESCAPE-TYPE SELF-CONTAINED BREATHING APPARATUS.

FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS:

SELF-CONTAINED BREATHING APPARATUS WITH FULL FACEPIECE OPERATED IN PRESSURE DEMAND OR OTHER POSITIVE PRESSURE MODE.

SUPPLIED-AIR RESPIRATOR WITH FULL FACEPIECE AND OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE PRESSURE MODE IN COMBINATION WITH AN AUXILIARY SELF-CONTAINED BREATHING APPARATUS OPERATED IN PRESSURE-DEMAND OR OTHER

DHS14300 FIFT OF GE OF

POSITIVE PRESSURE Mobil.

CLOTHING:

EMPLOYEE MUST WE'AR APPROPRIATE PROTECTIVE (IMPERVIOUS) CLOTHING AND EQUIPMENT TO PREVENT ANY POSSIBILITY OF SKIN CONTACT WITH THIS SUBSTANCE.

GLOVES:

EMPLOYEE MUST WEAR APPROPRIATE PROTECTIVE GLOVES TO PREVENT CONTACT WITH THIS SUBSTANCE.

EYE PROTECTION:
EMPLOYEE MUST WEAR SPLASH-PROOF OR DUST-RESISTANT SAFETY GOGGLES AND A
FACESHIELD TO PREVENT CONTACT WITH THIS SUBSTANCE.

WHERE THERE IS ANY POSSIBILITY THAT AN EMPLOYEE'S EYES MAY BE EXPOSED TO THIS SUBSTANCE, THE EMPLOYER SHALL PROVIDE AN EYE-WASH FOUNTAIN WITHIN THE IMMEDIATE WORK AREA FOR EMERGENCY USE.

